PHYSICS AND CHEMISTRY APPLIED TO FLOUR MILLING

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PHYSICS AND CHEMISTRY
APPLIED TO
FLOUR MILLING

BY

ARMAND J. H. HOUSSA

M.Sc. (Lond.)., A.I.C.

ASSISTANT LECTURER IN THE CHEMISTRY DEPARTMENT
BATTERSEA POLYTECHNIC, LONDON

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FOREWORD

Some time ago I was appointed a temporary inspector of the Board of Education to report upon the teaching of flour milling technology at the Battersea Polytechnic. There the science side of the course is called "Elementary Science applied to Flour Milling." It is based upon the syllabus for Flour Milling of the City and Guilds of London Institute, which had adopted the recommendations of the Technical Education Committee of the National Joint Industrial Council for the Flour Milling Industry. As chairman of the last-named committee, I knew that there was a demand for a text-book which would deal with certain science subjects more fully than existing trade literature, and less fully than available text-books which deal individually with the cognate science subjects. As a temporary inspector, I listened to some lectures delivered by the author on "Science applied to Flour Milling" and was very favourably impressed by their matter and manner. Accordingly I suggested to him that he should expand his notes for the lectures of the entire science course, and so provide a text-book of moderate size for the specialised subject.

I am glad to find that he adopted my suggestion. The work is his own; the comments I have made on his draft manuscript have been directed, almost exclusively, to the scope and form of the book. But I commend it to the attention and study of those who, primarily millers, are obliged to acquire a certain amount of scientific knowledge if they desire to understand the fundamental principles upon which many of their technical operations are based.

A. E. Humphries

Weybridge
June 4, 1929

PREFACE

This volume has been prepared primarily for students of flour milling who are pursuing a four-year course in milling for the examination of the City and Guilds of London Institute. The material dealt with in Part I covers the requirements of a student in the cognate subject necessary for the Second Year Intermediate Course, viz. elementary physics and chemistry. Part II deals with some aspects of organic chemistry. An effort has been made to present the subject-matter in a manner as simple and elementary as possible, consistent with the requirements of the syllabus laid down for the cognate subject in the Second Year Final Course.

In order to cater for the extremely specialised character of the subject, many important points will be found omitted, whilst others, admittedly out of place to a pure chemistry student of the same standard are included, e.g. an appendix is included dealing with hydrogen ion concentration and polarisation of light. The former is of great importance to flour milling chemistry, and it has been amply shown recently that consideration of " titratable acidity " alone is quite insufficient. Hence a brief explanation of the meaning of hydrogen ion concentration has been attempted. Likewise it is quite impossible to present a useful account of the sugars without introducing their optical rotatory power. Many critics may urge the futility of introducing students of only a limited scientific knowledge to such complex phenomena as polarised light and ionic concentration. Nevertheless it is the experience of the author that, if carefully introduced, the average student gains some understanding of them, though admittedly some fall by the wayside.

Inorganic chemistry is dealt with first, since all the fundamental laws and principles upon which the subject is based are more easily understood when viewed from an inorganic standpoint. Moreover, as a whole, inorganic compounds are less complex in their structure than organic compounds, particularly those organic compounds of interest to a flour milling student.

A flour milling student may wonder why he should concern himself with the complicated subject of organic chemistry. The reply to this is that the chemistry of flour is mainly organic, and that if he would understand the nature of the changes which go on in the various operations carried out in the industry he must learn at least something of organic chemistry.

The author is fully cognisant of the difficulties with which the average flour milling student has to contend in trying to cope with his Physics and Chemistry. The ordinary text-books contain an abundance of material from which he finds it difficult to sort out just the matter which is applicable to his particular needs. In this book the author has endeavoured to gather together the material to supply those needs. The contents of the book represent substantially the subject-matter of the course of lectures given by the author in Flour Milling Science at the Battersea Polytechnic during the last ten years. The material has been revised and brought up to date, in order to comply with the syllabus laid down by the City and Guilds of London Institute for their four-year course brought into operation in 1926. Where fuller details are required the student is recommended to consult one or other of the standard works dealing with flour milling chemistry, viz. Jago's *Technology of Breadmaking*, Kent-Jones's *Modern Cereal Chemistry*, Bailey's *Chemistry of Wheat Flour*. He will also find exceedingly useful the pamphlets published by the National Joint Industrial Council for the Flour Milling Industry ; in particular No. 3 published May 1929 entitled " Flour Quality, Its Nature and Control " by Dr. Fisher, Director of the Flour Milling Research Association.

In conclusion, the author desires to express his deep appreciation to various colleagues who rendered valuable assistance with the manuscript ; to Dr. A. E. Humphries for many helpful suggestions and criticisms, also his permission to use the figures and chart on page 112 ; to Dr. H. Hunter for the mode of presentation of the subject-matter in the chapter on Vapour Pressure and Hygrometry ; to Mr. G. E. Smith and Mr. T. E. G. Baker, B.Sc., for reading and correcting various parts of the manuscript.

Acknowledgments and thanks are also due to the City and Guilds of London Institute for permission to reprint the examination papers set in elementary physics and chemistry in 1927, 1928 and 1929; to H.M. Stationery Office for permission to reprint the analysis of wheat for the determination of fibre; to Messrs. E. R. and F. Turner, Ltd., the manufacturers of the Turner Washer, for permission to use Fig. 11; to Mr. C. Bentham for permission to reproduce Figs. 29, 30 and 31, and to Messrs. J. and A. Churchill for Figs. 48, 49 and 50 from Greenish's *Materia Medica*.

A. H.

Battersea Polytechnic
1929

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PHYSICS AND CHEMISTRY APPLIED TO FLOUR MILLING

PART I

CHAPTER I

THE SCOPE OF SCIENCE—FUNDAMENTAL PRINCIPLES—LAWS OF CHEMICAL COMBINATION

Science is usually described as "organised knowledge," i.e. an attempt to find out and know about the things which go on in the universe. Certain observations are made with respect to some natural occurrence or phenomenon, and attempts are made to arrange these observations in an orderly and systematic fashion. It is only when arranged in a systematic way that there is any possibility of deducing or arriving at any general law connecting the observed facts. From the general law deduced it is often possible to predict new facts, and these, when verified by observation, strengthen our faith in the law.

For the sake of convenience science is divided into a number of branches each dealing with some particular type of knowledge, e.g.:

(1) Botany is that branch of science which is concerned with the growth of plants and the changes taking place consequent on this growth.

(2) Physics has been described as the science of measurement, i.e. it deals with such things as the weight of a sack of flour, the temperature in a conditioner, the percentage moisture in the atmosphere, or the amount of heat required to boil water.

(3) Chemistry is concerned with the intimate nature of

things, the kind of matter composing them, and how bodies change when brought into contact with others. Chemistry is that branch of science dealing with the constitution of matter and the action and reaction of different kinds of matter on each other. The term "matter" embraces everything to be found in the universe, everything which has weight and occupies space. Thus the "stuff" which is termed matter is all around us. It will be obvious at first sight that there must be many different kinds of matter; for wood differs from glass and iron from water, yet all are kinds of matter and occupy space and have weight.

It is found that all kinds of matter can be classified under two main headings:

(*a*) Elementary or simple matter.
(*b*) Compound or combined matter.

The first class comprises all those substances which are composed entirely of fundamental particles of one kind, e.g. iron belongs to this class; this substance is composed solely of particles of the particular kind of fundamental matter with whose properties is associated the name "iron." Iron is a form of simple or elementary matter and it cannot be decomposed or broken down into any other kind of matter. Such a substance is termed an *element*. Examples of other elements with which a student of flour milling should be acquainted are oxygen, hydrogen, nitrogen, chlorine, carbon, sulphur, phosphorus, and those to be found on page 5.

The second class of kinds of matter comprises those substances which are composed of more than one kind of elementary matter or element, e.g. water; this has definite properties of its own, viz. it is a tasteless liquid. If attempts are made to split up water into simpler bodies it is found that this can be accomplished comparatively easily by passing an electric current through water containing a trace of sulphuric acid. This results in the decomposition of the water into two gases, namely, oxygen and hydrogen. These two gases are elements and cannot be decomposed further. Thus, water is a form of compound or combined matter composed of the elements oxygen and hydrogen combined in some specified proportion. Similarly starch and wood are forms of compound matter or compounds. Each is composed of the elements carbon,

hydrogen, and oxygen, but combined together in a different way.

All the materials to be found in the universe are thus either elements or chemical compounds, or mixtures of these. They exist in one or other of the three possible states of aggregation, i.e. solid, liquid or gaseous states.

Later it will be seen that flour is a mixture, a mixture of chemical compounds; whilst such substances as common salt, cream of tartar are single definite chemical compounds.

Fundamental Principles. Perhaps the first principle of fundamental importance with regard to matter is its "indestructibility." Matter can neither be created nor destroyed; the amount of matter in its various forms composing the universe is constant. We may alter the state of aggregation of a quantity of matter but its weight remains the same, e.g. we may convert water to steam but one pound of water will always yield one pound of steam, though of course its volume will be very much greater. Such a change, which is reversible, for we may condense the steam back to one pound of water, is termed a *physical change*, for we have but altered the state in which the matter exists.

On the other hand, if we cause a rearrangement of the particles of matter present in a particular compound, or if we cause particles of two kinds of elementary matter to unite, we are bringing about a *chemical change*, but the total quantity of matter we commence with is equal to the quantity we have at the end—we have only altered the type of matter.

An apparent contradiction to the principle of the "indestructibility of matter" is to be found in the burning of a candle or a piece of wood, paper or coal. It is a common practice, if we wish to get rid of something, to destroy it by burning it. But the material is not "destroyed" in the true sense: a piece of wood may be destroyed as wood, but all we really accomplish is a conversion of the materials composing the wood (largely two elements, carbon and hydrogen) into kinds of compound matter which happen to be gaseous and pass off unobserved into the atmosphere.

As will be seen later, the burning or combustion of a substance is a chemical process, whereby the elements composing that substance combine with oxygen (a gaseous element

present in the atmosphere), forming kinds of compound matter which may or may not be gaseous and which are called *oxides*. Thus, carbon unites with oxygen and yields carbon dioxide, a gaseous compound which passes into the atmosphere. Hydrogen unites with oxygen and yields water, which passes into the atmosphere in the form of vapour.

But if the whole of the products of combustion (namely, carbon dioxide and water) from the burning, say, of 1 gram of wood were secured and weighed, the weight obtained would be exactly the same as the weight of the original wood, plus the oxygen with which it has united.* The increase in weight due to combination with the wood will be exactly equal to the loss in weight suffered by the atmosphere. It is this *Law of Indestructibility of Matter* which enables us to represent chemical changes in the form of equations, for the weight of the original substances is equal to the weight of the final products, e.g. :

Weight of Carbon + Weight of Oxygen =
Weight of Carbon Dioxide produced.

The principle is perfectly general and applies to all chemical changes. Experiments have been carried out at various times to test the truth of this law, but, as far as we are able to measure and weigh, it is true. At one time the growth of a tree was supposed to be an exception, but in this instance no account was taken of the carbon dioxide assimilated by the plant from the atmosphere during its growth.

Physical and Chemical Change. Such changes as the conversion of water to steam, the solution of common salt in water, or the rendering of a piece of iron magnetic, are termed physical changes. The *kind* of matter is not altered, only the form or state of aggregation ; and if the force or agent causing the change be removed, it is perfectly easy to recover the original matter entirely unchanged.

On the other hand, a chemical change involves an alteration in the kind of matter, often a rearrangement of the particles or union with some other substance producing some entirely new kind of matter with distinct properties of its own. Moreover, such changes are permanent, and the original substance cannot be recovered except by another chemical operation.

* This assumes the wood has no ash.

Thus water can be decomposed by an electric current into its constituent elements, oxygen and hydrogen. Removal of the current does not cause the re-formation of the water. The oxygen and hydrogen can remain together mixed; it is only when they are exploded that water is re-formed.

Likewise when carbon burns, it forms carbon dioxide, a new kind of matter (compound matter with distinct properties of its own).

Thus a black solid, carbon, unites with a colourless gas, oxygen, and forms another entirely different gas, carbon dioxide, and by no known simple physical means is it possible to separate the carbon and the oxygen.

Chemical Combination. If the composition of bodies around us be examined, it is found that they can be divided up into a number of classes, viz.:

(*a*) Those bodies composed of fundamental or simple matter. The name given to substances falling in this class of bodies is *element*. There are over eighty of these elements known, and the whole universe is composed of these elements combined in various ways and proportions.

The elements are classified roughly into *metals* and *non-metals*, and are mostly solid substances, some gases, and a few liquids. Some of the common elements, with which a student of flour milling might be expected to have some acquaintance, are here appended:

NON-METALS		METALS	
Carbon	*Solids*	Iron	*Solids*
Sulphur		Copper	
Phosphorus		Lead	
		Silver	
Oxygen	*Gases*	Sodium	
Hydrogen		Potassium	
Nitrogen		Calcium	
Chlorine		Magnesium	
Bromine	*Liquid*	Mercury	*Liquid*

(*b*) Those bodies composed of more than one kind of simple matter combined according to the laws of chemical combination. Such bodies are termed *compound matter*, or simply

compounds. They are capable of being decomposed into their constituent elements by various chemical means. Thus the kind of matter which we call *water* is composed of two elements, oxygen and hydrogen, combined in definite invariable proportions. The process of decomposition to reveal the fundamental components of a substance is termed *analysis*. Also water can be formed from its elements by exploding hydrogen and oxygen together in suitable proportions. This " building up " of a compound from its component elements is termed *synthesis*. Water is termed a chemical compound, and it has a definite composition : 2 parts by weight of hydrogen united with 16 parts by weight of oxygen produce a kind of matter which we call " water." It has properties of its own, quite different from those of its constituent elements. The properties of the constituent elements become submerged in the new compound. Thus, water is a liquid while its constituent elements are both gases under ordinary conditions.

Many compounds are known, some containing two, others three and even four or five, different elements. For example, starch contains the elements carbon, hydrogen and oxygen, whilst gluten, in addition to these three elements, contains the element nitrogen.

Mixtures. Some substances on close examination are found to be merely physical mixtures either of elements or of compounds. One of the essential differences between a mixture and a definite chemical compound is that in a mixture the individual properties of the components are retained to an extent depending on the proportions present. Thus air is a mixture of a number of gases, chiefly nitrogen and oxygen with a small proportion of carbon dioxide.

The properties of air approach those of nitrogen more closely than those of oxygen, since nitrogen is present in air to the extent of nearly 80 per cent by volume. Thus the density of air is 14·5 whilst that of nitrogen and oxygen is 14 and 16 respectively. Likewise, in a mixture of iron and sulphur the individual properties of the two elements are retained, e.g.:

(*a*) The mixture is yellow in colour if much sulphur be present.

(*b*) The iron can be attracted out of the mixture by

means of a magnet, or the sulphur dissolved out with solvents.

(*c*) If examined under a microscope the individual light-coloured sulphur particles can be seen intermingled with the dark-coloured iron particles.

Thus the individuality of the iron and the sulphur is retained in the mixture, whilst in a compound of the two elements their properties become submerged in those of the compound formed, which has entirely distinct and characteristic properties. The compound formed by heating a mixture of iron and sulphur is termed iron sulphide, and its properties are quite distinct from those of a mere mixture of the two elements, e.g. :

(*a*) No iron or sulphur can be removed from the compound by a purely physical means, i.e. magnetic attraction or solubility.

(*b*) If examined under the microscope, the substance is found to consist of one kind of particle only, i.e. it is said to be homogeneous and consists of particles of iron sulphide only.

A mixture differs also fundamentally from a compound in its composition. A mixture may be made in almost any proportion desired. Innumerable mixtures of iron and sulphur, or sand and sugar, could be made, whereas only a limited number of definite chemical compounds of iron and sulphur can be produced, e.g. ferrous sulphide and iron pyrites. These compounds of iron and sulphur can only be produced (*a*) by uniting 32 parts by weight of sulphur with 56 parts of iron, (*b*) by uniting 64 parts of sulphur with 56 parts of iron. Attempts to make a compound of these two elements in any other proportion fail, the resulting body always containing 32 parts of sulphur *combined* with 56 parts of iron (or 64 parts of sulphur and 56 parts of iron), *mixed* with any excess of iron and sulphur that may have been used. (See Law of Constant Composition, p. 10.)

Considering air in the light of the foregoing properties of mixtures and compounds, it will be found that air is a mixture from the following considerations :

(*a*) Its composition, though remarkably constant, is not absolutely invariable, as slight divergences in the ratio of oxygen to nitrogen in samples of air from various sources can be observed.

(*b*) By liquefaction, and subsequent evaporation, it is possible to separate the oxygen from the nitrogen in air. This is a commercial method of obtaining supplies of these two gases.

(*c*) An " air " can be prepared by simply mixing oxygen and nitrogen in the proportions that they are present in air. No obvious change occurs on mixing, and no heat change or volume change occurs, such as usually accompanies a chemical reaction. Furthermore, the " artificial air " produced by the process mentioned has all the important properties of the natural variety.

It is of interest to compare air (a *mixture* of nitrogen and oxygen) with nitrogen peroxide (a compound of the same two elements), which is employed in the bleaching of flour.

The difference in properties between the two types of substance is here apparent. Air is relatively inert * with respect to bleaching qualities and is a colourless gas, whereas when the oxygen and nitrogen are united by submitting them to the action of an electric arc, the oxide of nitrogen produced is very active in its bleaching properties and it is brown in colour (nitrogen peroxide).

Further, it should be noted that flour itself is a mixture : it is a mixture of chemical compounds. For example, its composition is not absolutely invariable, the percentage moisture, starch, protein, etc., vary within certain limits.

Moreover, some of the constituents of the flour may be separated by a very simple physical process of washing ; the starch may be separated by washing through a piece of silk gauze.

* It should be noted in this respect that air possesses some bleaching qualities, for if a sample of flour be exposed to air for some time a whitening of the flour takes place. The process is referred to as the " ageing " or natural bleaching of flour, and may be due to traces of oxides of nitrogen in the atmosphere or due to direct oxidation of the colouring matter by the oxygen of the air.

Finally, if examined under a microscope, flour is obviously not homogeneous, i.e. there is present more than one kind of particle; starch cells and gluten particles and traces of fibre may be seen lying side by side.

SUMMARY OF GENERAL PROPERTIES OF MIXTURES AND COMPOUNDS

	Mixtures	*Compounds*
Composition	Variable, any composition being possible if substances are miscible.	Invariable.
Properties	Intermediate between those of constituents and approach those of the constituent present in greatest quantity.	Characteristic of the compound and independent of those of the constituents. The properties of constituents are submerged in compound formation.
Separation	Constituents often separable by purely physical means, e.g. salt can be separated from sand by dissolving out salt. Gluten can be separated roughly from flour by washing away starch, etc.	Constituents cannot be separated by physical means, and often only with difficulty by chemical means.
Appearance	*Heterogeneous*, i.e. composed of particles of more than one kind, e.g. flour viewed under the microscope; starch cells and gluten cells can be distinguished side by side.	*Homogeneous*, i.e. composed of particles of only one kind, e.g. common salt appears under the microscope as cubic crystals—all alike.

THE LAWS OF CHEMICAL COMBINATION

These laws embody actual observations on the mode in which elements unite with one another to form compounds.

The Law of Conservation of Matter. This states that matter can neither be created nor destroyed. The amount of matter composing the universe is constant, and all we can

do is to alter its form or state. Thus, if 12 lbs. of carbon be burnt it combines with oxygen from the air, forming carbon dioxide. The carbon dioxide formed weighs more than the original carbon dioxide by an amount exactly corresponding to the weight of oxygen combined with it ; 12 lbs. of carbon require 32 lbs. of oxygen to burn it completely and form 44 lbs. of carbon dioxide. The carbon dioxide formed is a colourless gas and passes into the atmosphere unobserved. We have not destroyed the carbon, but merely converted it into another less obvious form, namely, a gaseous form. The product still contains the 12 lbs. of carbon, but it is united by chemical forces with 32 lbs. of oxygen in the carbon dioxide.

We are enabled to represent this and all other definite chemical changes by means of an equation, thus :

Carbon + Oxygen = Carbon dioxide.

This expression for the moment tells us the mere fact that carbon and oxygen unite to form carbon dioxide. Later, by means of symbols, it will be found that the symbolic expression also represents the weights of carbon and oxygen which unite, viz. :

12 parts of Carbon + 32 parts of Oxygen = 44 parts of Carbon dioxide.

The Law of Constant Composition states that " any definite chemical compound always contains the same elements combined together in the same proportions by weight."

Thus the chemical compound which we know as water is composed of 2 parts of hydrogen united with 16 parts of oxygen (by weight); and the body produced has particular properties with which we associate the name water. Any other composition than 2 parts hydrogen to 16 parts oxygen would indicate a substance with different properties and therefore not water. Water can be formed by the union of 2 parts hydrogen and 16 parts oxygen, and no other proportions. If any excess over these proportions be present in a mixture which is exploded, then this excess will be left over uncombined. Thus water, no matter from where obtained, provided it be pure water, always contains the same elements combined together in the same proportions by weight.

This constancy of composition is perfectly general and is displayed by all chemical compounds.

The Law of Multiple Proportions. It is found that certain of the elements are capable of uniting in more than one proportion. This at first sight would seem to contradict the Law of Constant Composition, but this is not so, since two or more chemical compounds are produced *each* with a constant composition. Thus carbon and oxygen unite in two different proportions to form two different compounds, namely, carbon dioxide and carbon monoxide. The former is incombustible, the latter burns readily in air and forms the dioxide. The former has the composition 12 parts of carbon to 32 of oxygen (by weight), whilst the latter has but 16 parts of oxygen to 12 parts of carbon. This example illustrates the Law of Multiple Proportions, which states that :

" When two elements unite to form more than one compound the different weights of the one element combined with a fixed weight of the other bear a simple numerical relation to each other."

In carbon dioxide there are

32 parts of oxygen to 12 parts of carbon (by weight),

whilst in the monoxide there are

16 parts of oxygen to 12 parts of carbon (by weight).

The different weights of oxygen each combined with the same fixed weight of carbon (namely, 12 parts) are in the ratio of 32 : 16, i.e. 2 : 1, a simple numerical relationship as required by the law.

This law is quite universal and applies to all elements which combine to give more than one compound. Thus, nitrogen combines with oxygen in five different proportions to give the five oxides of nitrogen. In these the different weights of oxygen per unit weight of nitrogen are in the ratio 1 : 2 : 3 : 4 : 5.

These laws and others show us that the compounds of the universe are composed in an orderly, systematic way. These laws are the results of experimental observation and are therefore facts.

In order to understand why it is that elements combine in this fashion we must know something of the constitution of matter. Many ideas have been entertained with regard to the ultimate structure of matter ; even as far back as the time of the Greeks vague ideas were put forward as to how

things were constituted. These ancient views were amplified to some extent by John Dalton in 1803, and put forward as the so-called "Atomic Theory." This consists of a series of suppositions or assumptions with regard to the constitution of matter. The general purpose of a theory is to arrive at a series of statements we may suppose to be true. If these suppositions enable us to verify known facts and predict others, it may safely be concluded that the suppositions were correct. If not, then the theory must be modified or rejected.

The atomic theory of Dalton enables us to explain the facts, i.e. the laws of chemical combination, and it is concluded that the suppositions in it are correct. We have no experimental means at our disposal for confirming these suppositions. Modern work, however, on atomic structure, is supplying gradually this necessary experimental confirmation.

The suppositions of Dalton's theory are as follows :

(1) All matter is composed of a number of extremely minute indivisible particles which are called *atoms*.

These ultimate particles are so small as to be unweighable and invisible by all ordinary means. Fractions of atoms, of course, do not exist.

(2) Atoms of any one element are alike in size, shape, and weight, but different from the atoms of any other element.

(3) Compounds are formed by the union of atoms in simple proportions, e.g. **1 : 1, 1 : 2**, etc.

Thus an "atom" is the smallest particle of an element which can take part in a chemical change.

Some years after Dalton's time the word "molecule" was used to indicate the smallest particle of a compound.

Thus, 1 atom of carbon unites with 1 atom of oxygen, forming 1 molecule of carbon monoxide.

The word "molecule" is also applied to the particles produced by the union of two atoms of the *same* element. Ordinary oxygen is found to consist of particles which are molecules of oxygen, i.e. two atoms of oxygen linked together. Single atoms of gaseous elements do not usually exist by themselves.

Actually, nothing is required to be known of the absolute weights of any of the atoms, but if one be taken as standard, the weights of the others may be compared with it. Thus, the atom of oxygen is taken as having a weight of 16 units, or atomic weight 16, and the relative atomic weights of all the

other elements have been determined by comparing the weights of their atoms with that of oxygen.

In this way a table of atomic weights has been arrived at, of which some are given below.

Likewise for each element is employed a symbol. These symbols have been arrived at in various ways, some from the Greek names and some from the Latin names for the elements. The initial letter of the name of the element is used as the symbol, except where there are more than one element with the same initial letter, when the second letter of the name is used in addition to the first—the first letter being used in larger type and the second *always* in small type.

Potassium,	symbol	K,	from Latin	Kalium.
Sodium	,,	Na,	,, ,,	Natrium.
Iron,	,,	Fe,	,, ,,	Ferrum.
Copper,	,,	Cu,	,, ,,	Cuprum.
Mercury,	,,	Hg,	,, Greek	Hydrargyrum.
		etc.		

The following is a list of some of the commoner elements of interest to flour milling students, with their symbols and in order of their atomic weights :

ELEMENT	SYMBOL	RELATIVE ATOMIC WEIGHTS (nearest whole number)
Hydrogen	H	1
Carbon	C	12
Nitrogen	N	14
Oxygen	O	16 (*standard*)
*Sodium	Na	23
Phosphorus	P	31
Sulphur	S	32
Chlorine	Cl	35·5
Potassium	K	39
Calcium	Ca	40
Iron	Fe	56
Copper	Cu	63

* It will be noticed that with the exception of sodium the first seven elements of those given, i.e. the lighter ones, are all non-metals, whilst the heavier ones, the last four of those given, are metals.

The symbol of an element is intended to represent two things :

(1) It is a qualitative expression, i.e. it is merely a shorthand convenient mode of writing down the name of the element.

(2) It is a quantitative expression, since it represents a definite amount of that element, namely, one atom of definite relative weight. H represents one atom of hydrogen of unit weight ; H_2 represents two atoms or one molecule of hydrogen of two weight units. The total weight of such a particle is termed its molecular weight.

To represent a compound the symbols are written side by side, the numbers of each atom present (when more than one) being represented by a small figure appended to the right-hand bottom corner of the symbol. Thus :

HCl represents a molecule of hydrochloric acid (of $1 + 35{\cdot}5 = 36{\cdot}5$ weight units), i.e. a compound of 1 atom each of hydrogen and chlorine.

H_2O represents a molecule of water (of $2 + 16 = 18$ weight units), i.e. a compound of 2 atoms of hydrogen and 1 atom of oxygen.

$NaHCO_3$ represents a molecule of sodium bicarbonate (of $23 + 1 + 12 + 48 = 84$ weight units), i.e. a compound of 1 atom each of sodium, hydrogen, carbon, and 3 atoms of oxygen.

A number affixed in front of a group of symbols represents the number of times that group is to be considered, e.g. $2H_2O$ represents 2 molecules of water.

Chemical reactions are represented by means of equations. This is possible since the Law of Conservation of Mass tells us that the weight of reacting materials is always equal to the weight of the resulting products provided the whole of these be secured.

Thus a chemical equation tells us two things : it tells us in a shorthand form what products are formed when two things react ; also it tells us the weights of the reacting quantities, e.g. :

$$C + O_2 = CO_2$$

represents the complete burning of carbon, combination with oxygen, and formation of carbon dioxide. Also it tells us that :

1 atom of carbon (12 weight units) combines with 2 atoms of oxygen (32 weight units), and form 1 molecule of carbon dioxide (12 + 32 = 44 weight units) ;

or, taking 1 gram * as the weight unit,

12 gm. Carbon + 32 gm. Oxygen = 44 gm. Carbon dioxide.

The relation is equally true if the weight unit chosen is the ton or pound.

Such an equation enables us to calculate the weight of any one component produced or required, provided one other quantity is known.

12 gm. carbon require for complete combustion 32 gm. oxygen.

$\therefore$ 1,000 gm. „ „ „ „ „ $\frac{32}{12} \times 1000$ gm. oxygen

$= 2666{\cdot}6$ gm. oxygen.

Since one litre † of oxygen under normal conditions weighs $\cdot089 \times 16$ gm., ‡ 2666·6 gm. oxygen would occupy a volume of

$$\frac{1}{\cdot089 \times 16} \times 2666{\cdot}6 \text{ litres} = 1{,}872{\cdot}6 \text{ litres.}$$

As air contains only one-fifth of its volume of oxygen, this volume of oxygen would be present in $1872{\cdot}6 \times 5$ litres of air = 9,363·0 litres of air.

Thus we get the information that :

1 kilogram § of carbon (a little over 2 lbs.) requires for complete combustion to carbon dioxide 9,363·0 litres of air.

These matters assume some importance where questions of fuel economy are concerned, for the temperature of that enormous quantity of gas has to be raised to a fairly high degree in passing through the fuel bed.

The products of combustion (carbon dioxide and nitrogen, assuming theoretical combustion) carry a considerable

* See Chapter VI for weight units, etc.

† 1 litre = 1,000 cubic centimetres or c.c. (See Chapter VI.)

‡ Density of oxygen is 16 compared with hydrogen, and 1 litre of hydrogen weighs ·089 gm.

§ 1 kilogram = 1,000 gm.

quantity of heat which is lost unless some form of heat exchanger be employed to recover it.

Consider some of the chemical reactions involved in the artificial production of carbon dioxide in bread-making, etc.

(*a*) The decomposition of sodium bicarbonate on heating:

$$\underset{\text{sodium bicarbonate}}{2NaHCO_3} = \underset{\text{sodium carbonate}}{Na_2CO_3} + CO_2 + H_2O$$

Reacting weights:

$$2\{23+1+12+48\} = \{(2\times 23)+12+48\} + \{12+32\} + \{2+16\}$$
$$168 \qquad\qquad 106 \qquad\qquad 44 \qquad\qquad 18$$

From this it can be seen that on heating 168 gm. of sodium bicarbonate, 44 gm. of carbon dioxide are produced, and since 1 litre of carbon dioxide under normal conditions weighs $\cdot089 \times 22$ gm.,* 44 gm. of CO_2 would occupy $\frac{44}{\cdot089 \times 22} = 22{\cdot}4$ litres, so that 1 gm. of $NaHCO_3$ on heating would yield $\frac{22{\cdot}4}{168}$ litres $CO_2 = \cdot133$ litre = 133 cubic centimetres of CO_2.

(*b*) The decomposition of sodium bicarbonate by means of an acid substance, e.g. cream of tartar, i.e. potassium hydrogen tartrate, $KH(C_4H_4O_6)$:

$$KH(C_4H_4O_6) + NaHCO_3 = KNa(C_4H_4O_6) + CO_2 + H_2O.$$

Reacting weights:

$$\{39 + 1 + 4(12) + 4 + 6(16)\} + \{23 + 1 + 12 + 3(16)\} =$$
$$188 \qquad + \qquad 84$$
$$\{39 + 23 + 4(12) + 4 + 6(16)\} + \{12 + 2(16)\} + \{2 + 16\}$$
$$210 \qquad + \qquad 44 \qquad + \qquad 18$$

Thus the correct proportion in which cream of tartar and sodium bicarbonate must be mixed for complete reaction is 188 parts cream of tartar : 84 parts sodium bicarbonate.

These two substances are used in baking powder, a preparation which on treatment with warm water yields carbon

* Density of $CO_2 = 22$ compared with $H = 1$, and 1 litre of hydrogen weighs ·089 gm.

dioxide.* This is one of the methods of obtaining the carbon dioxide necessary for the raising of dough in the making of cakes. The necessary reagents—sodium bicarbonate and a substance of an acid nature, like cream of tartar—are mixed in with the flour in the requisite proportion. Such a flour is termed "self-raising" flour, for cakes or bread can be made from it without the aid of yeast. The bread obtained is said to be "artificially aerated."

From the reacting quantities it can be seen that from 188 + 84 gm. of mixture, i.e. 272 gm. of baking powder mixture, can be obtained on suitable treatment with water as much carbon dioxide as can be obtained by heating 168 gm. of sodium bicarbonate alone.

When the cream of tartar mixture is used, the residue left in the article is sodium potassium tartrate or Rochelle salts—a substance left in such small quantities as to be perfectly harmless. Since

272 gm. of baking powder mixture yield 22·4 litres CO_2

1 gm. " " " " $\frac{22{\cdot}4}{272}$ " "

$= {\cdot}082$ litres,

$= 82$ c.c. CO_2.

Another acid agent often employed in place of the cream of tartar is acid calcium phosphate, $Ca(H_2PO_4)_2$:

$$Ca(H_2PO_4)_2 + 2NaHCO_3 = Ca(NaHPO_4)_2 + 2H_2O + 2CO_2$$

From this equation the reacting quantities can be calculated exactly as in the previous example.

CHAPTER II

THE ATMOSPHERE—OXYGEN—HYDROGEN—WATER

THE ATMOSPHERE

THE name atmosphere is given to the gaseous envelope which surrounds the earth.

* The mixture of the two substances, if kept perfectly dry, undergoes no change. Rice starch is often added to the mixture to assist the materials to keep dry.

Close acquaintance with air often tends to make us disregard its presence, even though we depend for our existence on it. The ancient philosophers had difficulty in appreciating the material nature of air, possibly because it is a gas, a form of matter less obvious than solids or liquids.

Thus, though the air is an invisible gas, or rather a mixture of gases, yet it is a material substance and has a definite weight. This was determined by philosophers in the seventeenth century, and we know that in London 1 litre of dry air weighs approximately 1·293 gm. at N.T.P.* Also this mass of air above the earth exerts a pressure on its surface, something of the order of 14·7 lbs. on every square inch of surface. This pressure, which is termed the *atmospheric pressure*, varies from place to place according to height above sea-level, gradually getting less as we ascend where there is less air above us and greater as we descend. Likewise the atmospheric pressure varies from day to day during the different seasons of the year according to climatic conditions, the presence of much water vapour, etc. The instrument used for measuring the pressure of the atmosphere consists of a long tube filled with mercury and inverted in a trough of mercury (Fig. 1); the quantity of mercury in the column being supported by the pressure of the air on the mercury in the trough. Thus the height of the mercury column is a measure of the atmospheric pressure, and is usually of the order of 30 ins. or 76 cm. at sea-level.

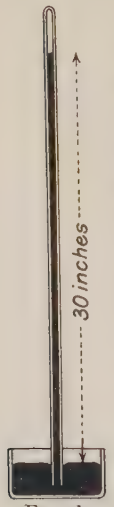


FIG. 1

It has been stated that air is a mixture. It is a mixture of a number of substances, but the two main constituents are the elements oxygen and nitrogen. These are present in the approximate ratio 1 : 4 by volume, but whilst the percentage composition of the atmosphere is fairly constant it is not absolutely so.

Of these two constituents oxygen is the most important and is referred to as the active constituent, whilst the nitrogen is relatively inert and is termed the inactive constituent.

* N.T.P. = normal temperature and pressure, 0° C. and 760 mm. of mercury.

The Part played by the Oxygen in the Atmosphere.

1. Whenever a substance burns in air it uses up and combines with the oxygen, leaving the nitrogen behind; e.g. coke burns in air, uses up oxygen, and forms carbon dioxide. This is termed the "product of combustion," and passes up the chimney along with the remaining nitrogen and any excess air:

Carbon + Air (oxygen and nitrogen) ⟶ Carbon dioxide + Nitrogen.

Similarly coal, coal gas, wood, paper—all of which contain the element carbon as the main constituent—produce carbon dioxide on combustion which passes off into the atmosphere.

2. Oxygen plays an extremely important part in the respiration of all animals (and plants too). All animals when they breathe take air into the lungs; here the oxygen, or part of it, is absorbed in the blood stream which transports it to various parts of the body where it oxidises waste tissue. Since the essential constituent of tissue is carbon it is oxidised to carbon dioxide. This oxidation of waste tissue is essential to life, as accumulation of it results in the death of the animal. Oxidation or slow combination of the waste tissues produces heat in the same way that a piece of burning coal does, but in the latter the heat is evolved in a short space of time and produces a flame, whereas in the former the evolution of heat is gradual and serves to keep the body temperature up. The products of respiration of animals then are nitrogen, carbon dioxide and excess air. Thus respired air contains more carbon dioxide than ordinary air, and unless efficient ventilation be employed to remove the carbon dioxide from a room it tends to accumulate till it reaches almost 10 parts CO_2 per 10,000 parts air.

ANALYSIS OF AIR

Ordinary air	*Expired air*
79·03 % N	79·03 % N
20·94 % O_2	16·99 % O_2
·03 % CO_2	3·98 % CO_2

The presence of carbon dioxide in ordinary air or expired air can be demonstrated by exposing to it some clear lime water. The lime water and the carbon dioxide in the air

react and form insoluble chalk, which is produced as a finely divided white precipitate, or often only as a cloudiness if a little carbon dioxide be present. There is present also in both ordinary and respired air variable amounts of water vapour. Plants also suffer changes similar to respiration in animals, and take in oxygen over the whole surface of their leaves and give off carbon dioxide; but this process of respiration is masked during the daytime by the process of carbon assimilation. This is a feeding process whereby carbon dioxide is taken in, chiefly through the leaves. Under the influence of sunlight and chlorophyll (the green colouring matter of plants), the carbon dioxide and water present in the plant are built up into complex compounds (carbohydrates—substances of the nature of starch, sugar, etc.), and oxygen is given off in the process. This process is termed "photosynthesis." (See Appendix, page 127.)

Carbon dioxide + Water = Formaldehyde + Oxygen
↓
More complex bodies
like starch and sugar.

Thus the wheat plant elaborates from carbon dioxide and water considerable quantities of starch which it stores up in the young grain against the time when the grain itself will commence to grow, then it has a ready-made supply of food at hand, namely, the starch.

In a general way the carbon dioxide evolved by combustion and respiration of animals is used up by plants in growing, so that the amount of carbon dioxide in the atmosphere remains approximately constant, usually about 3 parts of carbon dioxide per 10,000 parts of air.

In addition to oxygen, nitrogen and carbon dioxide, the atmosphere usually contains water vapour. This arises from the evaporation of water from the sea, lakes, and any exposed wet object and also results from the combustion of some substances containing hydrogen:

Hydrogen + Oxygen = Hydrogen oxide (water).

The amount of water vapour to be found in the atmosphere varies in different parts of the earth. It also varies with the temperature of the atmosphere.

In addition to the substances already mentioned as being

present in the atmosphere there are always traces of other substances in amounts varying with local conditions, e.g. in the air near the sea there are traces of common salt to be found due to spray from the sea. In industrial centres more or less sulphur compounds such as sulphur dioxide and sulphuretted hydrogen are always to be found. These arise usually from the combustion of coal which usually contains traces of sulphur.

Under certain circumstances, e.g. after a thunderstorm, traces of nitric acid are to be found (formed by union of oxygen and nitrogen under the influence of lightning). These traces of acid are neutralised by ammonia present in minute quantities as a result of decomposition of organic nitrogen compounds on the earth, and the resulting ammonium nitrate is washed out of the atmosphere by rain, thus helping to replenish the soil with nitrogen compounds.

The atmosphere always contains more or less fine dust, wind-blown sand particles and certain micro-organisms. The varieties of micro-organisms to be found are numerous, some harmful and others innocuous. Even yeast cells are to be found floating about in the atmosphere.

OXYGEN

The name oxygen means " acid former." It is an element which occurs abundantly in the free state in the atmosphere (approximately 20 per cent by volume) and also combined in many compounds, e.g. oxides.

PREPARATION. On a commercial scale it is obtained by the liquefaction and subsequent careful evaporation of liquid air.

Air, after removal of water vapour, carbon dioxide, etc., is liquefied by cooling it, under pressure. The liquid air so obtained is then allowed slowly to evaporate by releasing the pressure, when the nitrogen boils off first * and is pumped away and stored in cylinders under pressure. It is used in the production of synthetic ammonia and nitric acid. The oxygen likewise is stored in cylinders under pressure.

Oxygen may also be obtained on a commercial scale by the

* B.Pt. oxygen, −182·5° 3. B.Pt. nitrogen, −196·4° C.

electrolysis of water (or dilute alkali). Here the other product is hydrogen, which also is used in the production of synthetic ammonia and in the hardening of fats for margarine manufacture.

PROPERTIES OF OXYGEN. Oxygen is a colourless gas slightly heavier than air and slightly soluble in water (fishes make use of dissolved oxygen in their respiration). It is the chief agent in all combustion. When an element burns in air it unites with the oxygen in the air, forming an oxide. Non-metals like sulphur, phosphorus and carbon form oxides which are acidic in character.

If combination with oxygen is accompanied by flame the term *combustion* is used ; if unaccompanied by flame then the process is called *oxidation* or *rusting*, e.g. the rusting of iron is a combination of iron with oxygen.

Some substances catch fire spontaneously in air when in a state of extremely fine division. This is due to rapid oxidation and production of heat, giving rise to final ignition. Fires in flour mills have sometimes been ascribed to the presence of very fine flour particles in suspension in air ignited by a spark. Similar phenomena occur in coal mines.

Oxygen is essential to the respiration of all animals and also plants.

USES OF OXYGEN.

(1) With hydrogen or acetylene in oxy-hydrogen or oxy-acetylene flames which give extremely high temperatures and are used for cutting iron plates.

(2) In various breathing apparatus for use in submarines, aeroplanes at high altitudes, and also medicinally.

OXIDES.

Oxygen combines with most elements, yielding compounds called oxides ; some are gaseous, some solid. *Non-metals* yield oxides which are acidic and, with water, form acids, e.g. :

Carbon → Carbon dioxide → Carbonic acid.
Phosphorus → Phosphorus pentoxide → Phosphoric acid.

Metals yield oxides which are basic, i.e. react with acids, forming salts and water, e.g. :

Calcium → Calcium oxide (lime) which with Acids → Calcium salts.

HYDROGEN

Hydrogen, like oxygen, is an element. It is the lightest element known. Hydrogen does not occur free in anything but minute quantities on the earth, but is abundantly present in the sun and stars. Combined, it occurs abundantly in the form of water, and with carbon in many vegetable and animal substances, e.g. starch is composed of the elements carbon, hydrogen, and oxygen united together in definite proportion by weight. Hydrogen is also present in combined form in coal, mineral oils, and as one of the gaseous constituents of the mixture called coal gas.

Commercial Production of Hydrogen.

(1) By decomposition of water in form of steam by red-hot iron:

Water + Iron = Hydrogen + Oxide of Iron.

(2) By electrolysis (i.e. decomposition by means of an electric current) of water (or dilute solutions of alkali).

(3) From water gas, a mixture of hydrogen and carbon monoxide obtained by decomposition of water in form of steam by means of red-hot coke at 1,000° C.:

Water + Coke = Hydrogen + Carbon monoxide.

The hydrogen is obtained from water gas by separating the carbon monoxide by liquefaction.

On a laboratory scale hydrogen may be prepared by the action of dilute acids upon certain metals, e.g.:

Iron + Sulphuric acid = Iron sulphate + Hydrogen.

It will be seen later that an acid is a body containing hydrogen which can be displaced by a metal.

Properties of Hydrogen.

Physical. Colourless, odourless gas. Fourteen times lighter than air (hence its use in balloons and airships); 1 litre of hydrogen at normal temperature and pressure (0° C., and 760 mm.) weighs ·089 gm.

Chemical. Hydrogen combines with many other elements, e.g. combines with oxygen forming hydrogen oxide (water). Burns in air combining with oxygen to form water. The

flame of burning hydrogen in oxygen reaches a temperature of over 2,800° C.* (i.e. a vigorous chemical action occurs accompanied by enormous heat evolution).

Mixed with oxygen in the ratio of two volumes hydrogen to one volume oxygen it forms an explosive mixture, likewise two volumes of hydrogen and five volumes of air form an explosive mixture because air contains one-fifth its volume of oxygen.

INDUSTRIAL USES OF HYDROGEN.

(1) In the oxy-hydrogen blowpipe flame, the high temperature obtained is used for welding metals.

(2) In aeronautics for filling balloons and airships, owing to its low density.

(3) For the synthesis of ammonia by union with nitrogen.

(4) In the form of water gas, as a gaseous fuel. Hydrogen is also present to the extent of 50 per cent in ordinary coal gas.

WATER

It has been stated that when hydrogen burns in air or oxygen, i.e. when it combines with oxygen, water is produced. From this it follows that, chemically, water must be regarded as hydrogen oxide:

Hydrogen + Oxygen = Hydrogen oxide (or water).

This important fact—that hydrogen and oxygen unite and form water *only*—was first demonstrated by the celebrated chemist Cavendish in 1781.

The process whereby a compound is formed or built up from its component elements is termed *synthesis*. Thus in 1781 Cavendish synthesised water from its elements and found it had all the properties of water which occurs naturally.

Later the composition of water was confirmed by *analysis*, i.e. a process whereby a compound is split up or decomposed into its component elements. Water was analysed by decomposing steam with red-hot iron and the amounts of oxygen and hydrogen determined. Water may also be analysed by electrolysis.

In the nineteenth century † the composition of water by weight was determined as being 11·23 per cent hydrogen,

* Hence its use in oxy-hydrogen blowpipe flame. † Dumas, 1843.

88·77 per cent oxygen, or one-ninth hydrogen and eighth-ninths oxygen, whilst that by volume determined by electrolysis was 66·67 per cent hydrogen, 33·33 per cent oxygen or 2 volumes of hydrogen to 1 volume of oxygen.

Water is found abundantly in nature as spring, river, lake, and sea water, and also as water vapour in the atmosphere and in the form of clouds. It is estimated that three-fourths of the earth's surface is covered by water.

The water droplets composing clouds can be regarded as practically pure water, whilst all the other forms of natural water contain dissolved gases and solids. Thus rain in its passage through the atmosphere dissolves the component gases of air approximately in the proportion of their solubilities. The one which has the most important effect is the carbon dioxide so dissolved.

PROPERTIES OF WATER. When pure it is a colourless, odourless, tasteless liquid, slightly blue in colour if viewed in thick layers. It freezes to ice at 0° C. and boils, forming steam at 100° C. at atmospheric pressure. At increased pressure the boiling point is higher. At 4° C., 1 c.c. of water weighs 1 gm., i.e. its density is unity. Between this temperature and 0° C. it expands slightly, so that at 0° C. 1 gm. of water occupies 1·000122 c.c. and its density is less than unity.* Likewise from 4° C. upwards water expands, the density thereby diminishing. Thus at 4° C., water has its maximum density, and at no other temperature is its density unity but always something less. Water at 4° C. is taken as the standard of reference for the density of solids and liquids. Further, when water is converted to ice, an expansion occurs and 1 gm. of ice occupies 1·09083 c.c.† Thus its density is much less than that of water, and it therefore floats on water. (The increase in volume on ice formation is approximately one-eleventh.) Likewise, water on conversion to steam suffers an enormous expansion, 1 c.c. of water at 100° C. yields 1,579 c.c. of steam. Thus the density of steam compared to water would be very small; so that a smaller unit of density is chosen, i.e. either that of hydrogen or air. The densities of all gases are referred

* Density $= \frac{\text{mass}}{\text{volume}}$; $\therefore$ Density of water = 0·999877 at 0° C.

† Density of ice at 0° C. = 0·91674.

to either hydrogen or air and the density of steam referred to hydrogen is 9 and referred to air is ·622.

Solvent Power of Water. One of the outstanding properties of water is its extensive solvent power, i.e. its ability to dissolve other substances, either gaseous, solid or liquid.

If common salt be thrown into water, it dissolves, i.e. it apparently disappears as solid salt and passes into solution. The change which occurs is a physical one, since all the salt can be recovered unchanged by evaporating off the water. This phenomenon of solution is displayed by a large number of substances, the material dissolved being termed the *solute*—the material in which the solute dissolves the *solvent*, whilst the resulting material is termed a *solution*.

Water is the commonest (but not the only) solvent we know, and it is due to its remarkable solvent action that chemically pure water is never found in nature and never enters into domestic or industrial use. Water that is found in nature invariably contains substances in solution, and often suspended insoluble substances as well. The nature of the substances in solution depends largely on the history of the water, the region from which it is drawn, and the nature of the soil through which the water has passed.

Roughly we may classify natural waters as follows :

(1) Rain water,
(2) Surface water (lakes, rivers, etc.),
(3) Ground water (springs and wells),
(4) Sea water,

whilst the dissolved or extraneous material present can be classified as :

(*a*) Substances arising from contamination with sewage—liable to render the presence of injurious micro-organisms possible, also organic nitrogenous compounds, ammonium salts, nitrites and nitrates.

(*b*) Dissolved solids, chiefly calcium, magnesium, and sodium salts.

(*c*) Suspended matter, e.g. mud, etc.

Of these, water in class (*a*) should never be used for domestic or industrial purposes, whilst water in class (*b*) is quite harmless for drinking purposes but often requires to be specially

treated for some industrial uses, and class (*c*) may be readily purified by settling or filtering.

Rain Water. This, as it passes through the atmosphere, dissolves air, small quantities of solids (products of combustion), and also carries down with it dust and micro-organisms. Even so, it is the purest form of natural water, and can be used for almost any purpose provided it can be obtained in sufficiently large quantity.

Surface Water, which flows into streams, lakes, and rivers, may resemble rain water if it has passed over a surface of insoluble material, e.g. granite, but more often surface water contains varying amounts of compounds of sodium, calcium, and magnesium, taken up by direct solution from the soil over which it has passed. In addition it usually contains suspended insoluble material, mud, etc., eroded from the banks of rivers. The suspended matter can readily be removed by filtration or settling in tanks ; and provided the water has not been polluted by sewage it is useful for many industrial purposes without further purification, e.g. washing wheat.

Ground water may be obtained from springs or wells. It contains, like surface water, dissolved calcium, magnesium, and sodium compounds, but if from deep wells is free from sewage pollution and by reason of the depth to which it has filtered is usually of quite high purity and suitable for drinking purposes.

Sea water contains in addition to the usual compounds to be found dissolved in water approximately 3 per cent of common salt.

The suspended matter and substances arising from contamination with sewage are usually removed in the ordinary processes of purification of water, and most water from supply systems contains only dissolved solids and gases which, provided they are not present in excess, are quite harmless and the water is fit for most domestic uses.

The presence, however, of these dissolved mineral compounds has an important effect when the water is used for certain industrial purposes, e.g. steam raising or for laundry work.

HARD AND SOFT WATER. Water containing appreciable quantities of dissolved compounds is said to be *hard*, whilst

one in which they are absent or present to only a very limited extent is said to be *soft*. The chief compounds causing the hardness of water are :

(1) The bicarbonates of calcium and magnesium,

(2) The sulphates of calcium and magnesium, and

(3) The chlorides of calcium and magnesium together with traces of other salts.

The sulphates and chlorides find their way into the water by direct solution from the soils over or through which the water has passed ; whilst the bicarbonates are only present in water arising from chalky districts. Here the rain water containing dissolved carbon dioxide, flowing over chalk, converts this insoluble material to a soluble compound, calcium bicarbonate. Similar remarks apply to magnesium bicarbonate from magnesium carbonate which always occurs along with chalk (calcium carbonate).

Thus :

Calcium carbonate + Carbon dioxide and Water → Calcium bicarbonate
(chalk, insoluble) (soluble)

This change from insoluble calcium carbonate to soluble bicarbonate can readily be demonstrated in the laboratory by passing a stream of carbon dioxide through clear lime water. This produces a turbidity in the solution due to the precipitation of calcium carbonate in a finely divided condition :

Calcium hydroxide + Carbon dioxide = Calcium carbonate + Water
(lime water) (insoluble chalk)

On continued passing of the stream of carbon dioxide, the turbidity vanishes and a clear solution containing calcium bicarbonate is produced. The presence of calcium bicarbonate in this solution and incidentally in London tap water can be shown by boiling the water, when the bicarbonate decomposes, depositing again insoluble chalk and evolving carbon dioxide :

Calcium bicarbonate → Calcium carbonate + Carbon dioxide + Water

This deposit of chalk can be observed inside a domestic kettle where it accumulates and is commonly termed " fur," whilst in the case of boilers it is termed " boiler scale." The accumulation of scale is undesirable as it lowers the efficiency of the boiler and wastes heat ; usually the scale is not allowed to form, by softening the water, i.e. removing the magnesium

and calcium compounds before the water is allowed to pass into the boiler.

Soft water forms a lather readily with a soap solution, whilst hard water forms a lather only with difficulty or after using much soap solution. This forms a means of determining the hardness of a sample of water, a method known as *Clarke's Method* and depending on the following facts :

Common soap is a mixture of three chemical compounds all soluble in water, viz. sodium oleate, sodium palmitate, and sodium stearate, and is made from fats composed of compounds related to these three substances. When water containing calcium or magnesium compounds in solution is brought in contact with common soap a chemical reaction sets in, and the calcium in solution in the water exchanges place with the sodium of the soap. The change is called a *double decomposition* and involves a rearrangement of the particles of matter present with the production of calcium oleate, calcium palmitate, and calcium stearate (which are insoluble in water and thrown out as a " scum " or precipitate) and sodium compounds which remain in the water. Thus :

Sodium oleate Sodium palmitate Sodium stearate (soluble)	and Calcium compounds in Water	→	Calcium oleate Calcium palmitate Calcium stearate (insoluble)	and Sodium compounds

Thus it can be seen that the calcium compounds react with the soap, forming a scum, and thereby preventing it from accomplishing its normal function, i.e. forming a lather, with which is associated its detergent or washing action.

Further, the harder a sample of water or the more calcium compounds it contains, the more soap will be required before a lather can be produced. Theoretically, a soft water, with no hardness, should not require any soap to soften it, but actually a small amount of soap is always required to form the bubbles composing the lather.

Hardness may be measured in terms of the volume of a standard soap solution required just to form a lather with a given volume of water, usually 100 c.c. The soap solution is standardised against 100 c.c. of water of known prepared hardness. The hardness of the water can then be expressed as containing so many grains of calcium carbonate per gallon or as parts of calcium carbonate per 100,000 parts of water.

This method rapidly gives the amount of dissolved compounds causing the hardness to a degree of accuracy sufficient to enable them to be removed efficiently. An exact knowledge of the quantity of each of the different compounds present is not required, the whole being determined by Clarke's soap solution method and expressed as calcium carbonate.

Since the presence of these compounds of calcium and magnesium is for some industrial purposes undesirable, they are removed, i.e. the water is softened. Particularly is this the case where the only water available for steam-raising or laundry work is hard water.

Methods of Water Softening.

(1) It is found that if London tap water, which contains on an average dissolved compounds chemically equivalent to about 24 parts of calcium carbonate per 100,000 parts of water, be boiled, its hardness is reduced to about 7 parts per 100,000.* Any further boiling fails to reduce the hardness below this value, and the completion of the softening must be done by means of chemical reagents.

This method of boiling is never used on a commercial scale for softening as it is uneconomical to use heat for the purpose when it can be accomplished by cheaper chemical means.

The hardness which is removed by boiling is termed *temporary hardness* and that remaining after boiling *permanent hardness*. The former is caused by the presence in the water of bicarbonate of magnesium and calcium, whilst the latter is due to sulphates and chlorides of calcium and magnesium.

The bicarbonates are decomposed by heating, yielding insoluble chalk, thus removing the cause of the hardness, while the sulphates and chlorides are unaffected by boiling.

(2) To remove the temporary hardness on a commercial scale chemical means are adopted. Milk of lime (calcium hydroxide) is added to the water in quantity calculated to be sufficient to convert all the bicarbonate to carbonate according to the equation :

$Ca(HCO_3)_2$	+	$Ca(OH)_2$	=	$2CaCO_3$	+	$2H_2O$
Calcium bicarbonate (soluble)	+	Slaked lime	=	Chalk (insoluble)		Water

* London tap water : Temporary hardness, 17 parts $CaCO_3$/100,000.
Permanent hardness, 7 parts/100,000.

Calcium bicarbonate can be regarded as being composed of calcium carbonate, carbon dioxide and water. The addition of lime results in a combination of the carbon dioxide with lime, forming insoluble chalk; and the bicarbonate, having lost its carbon dioxide, is reconverted into chalk and water:

$$Ca(HCO_3)_2 = CaCO_3 + CO_2 + H_2O$$
$$CO_2 + Ca(OH)_2 = CaCO_3 + H_2O$$

Compare this with the previous equation. The precipitated chalk forms a sludge which is removed from the water by filtration through a bed of sand.

(3) Compounds causing the permanent hardness, usually sulphates and chloride of calcium and magnesium, are removed in a similar manner by the addition of the calculated quantity of sodium carbonate. This interacts as follows:

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$
$$MgSO_4 + Na_2CO_3 = MgCO_3 + Na_2SO_4$$

(precipitated) (left in solution)

insoluble carbonates being produced, leaving in solution a sodium salt which has no effect on the hardness of the water.

The operation of water softening is carried out in many industries, usually by a plant which is automatic and continuous. The calculated amount of lime, in form of milk of lime, sufficient to remove the temporary hardness, and the calculated amount of sodium carbonate solution sufficient to remove the permanent hardness are tipped at regular intervals automatically into a known volume of water. The whole is agitated and the sludge of calcium carbonate is filtered on to a bed of sand. The water passes to the soft water storage, whilst a fresh supply of hard water flows into the apparatus and is treated as before.

(4) In addition to these methods, a method in common use now is the *Permutite Process*. Permutite is a naturally occurring mineral belonging to a class of substances called "zeolites," which are hydrated silicates of sodium and aluminium. The substance is now made artificially. The water is softened by allowing it to flow over the fine granular material, when calcium takes the place of sodium in the zeolite, leaving harmless sodium salts in solution.

When the zeolite has absorbed a large quantity of calcium

it becomes ineffective, and is regenerated by treatment with a concentrated solution of sodium chloride (common salt), after which the zeolite can be again used as a water softener.

Sodium compounds + "zeolite" (permutite) + Calcium compounds = Sodium compounds + Calcium "zeolite"

Calcium "zeolite" + Sodium chloride = Sodium "zeolite" + Calcium chloride

Water for Wheat Washing. The degree of purity required of water for wheat washing is much lower than that required for drinking purposes. Provided that the supply is free from suspended particles and also organic impurity, indicating recent contamination with sewage, almost any water can be used. Many mills use river or canal water, whilst some have an artesian well of their own from which they can draw an almost unlimited supply of clear bright water. Where, however, the available supply of water is small, the same or part of the water may be used over and over again. A small supply of clean water is run into the water in the washer and an equal amount of dirty water run to waste. The fresh supply is regulated to keep the washing water as "clean" as desired. The use of town supply drinking water is, of course, costly but it is sometimes employed.

The amount of water used, and the time it is allowed to remain in contact with the wheat, varies of course with the kind of wheat being treated. Soft damp grains require to be washed rapidly, whilst dirty hard grains require slow washing and more than one wetting. Where a miller blends several varieties of wheat, as is usual in this country, he may find it necessary to treat the constituents of his mixture separately according to their nature, the harder, drier varieties being subjected perhaps to two washings, whilst the soft weak wheats are given only a light washing. The final desired moisture content of the wheat must also be borne in mind when deciding how to wash the constituents of a particular mixture.

Water penetrates into the wheat grain to an extent depending on the nature of the grain; soft weak wheat absorbs and retains moisture fairly readily, e.g. Australian wheats; whilst the hard horny varieties absorb little and retain but small

quantities on their coats unless treated more than once or for prolonged periods.

Such resistant wheats are often treated in a steamer before washing or as an alternative treated with warm water, e.g. Karachi and Durum wheats. The " hardness " of the washing water is stated to affect the extent to which moisture penetrates into the grain. This may be due either to the formation of an impervious coating on the grain which prevents softening, or to the fact that some wheats already have a filmy greasy coating that hard water cannot penetrate.

Moisture in Wheat and Flour. It is well known that the moisture content of wheats from various parts of the world varies over a fairly wide range and depends largely on the climate of the country in which they were grown. It varies from about 9 per cent for Indian wheat to 16 to 18 per cent for average English wheat. It is somewhat doubtful how and where the moisture is present in the grain, but probably it is present in two forms :

(1) So-called " hygroscopic " moisture, which adheres to the particles, as sand absorbs water. This moisture has little or no effect on the chemical composition of the flour and is easily removed. Methods of moisture-testing aim at removing just this moisture.

(2) So-called " moisture of constitution," forming a definite part of the protein molecule. This moisture, sometimes called " water of hydration," is removed only with difficulty, and when removed profound changes are brought about in the character and constitution of the flour. Moreover, the moisture cannot be replaced to reproduce the original flour.

For moisture-testing purposes it is only required to remove (1), but unfortunately no method is available which indicates just when (1) has been completely removed, and (2) commences to be lost. Probably the loss of (2) commences before the completion of the loss of (1). This possibly accounts for the divergence in the results obtained for the percentage moisture in a sample of flour as determined by various investigators. Each carries out the determination under different conditions, and whilst any one set of determinations are consistent among themselves, as a whole the values do not agree.

The value returned for the percentage moisture in a sample

of wheat or flour varies according to the method employed or according to (*a*) the temperature employed, (*b*) the time of heating, (*c*) the type of oven employed, (*d*) the vessels used.

The variation can be observed in the following series of figures for percentage moisture in flour carried out by four different methods (*Cereal Chemistry*, Sept. 1925). The vessels used were in all cases identical, viz. aluminium dishes, cylindrical in shape, 18 mm. high and 60 mm. diameter, with close-fitting lids ; 2 gm. of flour were used in each case, a thoroughly representative sample of a spring wheat flour.

	Oven	*Temperature*	*Time*	*Percentage Moisture*
A	Vacuum 28 mm. mercury pressure	98°–100° C.	5 hours	13·38*
B	Air	130°	1 hour	13·25
C	Air	125°	1 hour	13·22
D	Air	135°	1 hour	13·31

Thus it will be seen that the vacuum oven gives for the percentage moisture higher results than the air oven. This seems to be due to the absence of air in contact with the sample, since it has been shown that when a sample of flour is heated in air it loses water rapidly at first. Then the rate of decrease in weight diminishes, and finally further heating results in an actual gain in weight due to oxidation of some of the flour components, possibly the fat. This increase in weight of such a sample can be seen from the following figures :

Water oven, temperature 98·5° C., 5 gm. flour used.
Initial weight of dish + 5 gm. flour . . . . 22·5477 gm.
After 4 hours heating . . . . . 21·8766 gm.
(corresponding to a loss of 13·42 per cent)
After 6 hours heating . . . . . 21·8864 gm.
„ 8 „ „ . . . . . 21·8878 gm.
(corresponding to a loss of 13·20 per cent)

The use of the vacuum oven obviates this increase in weight due to air oxidation.

* These figures are the average of four tests carried out by about twenty collaborators.

From what has been quoted it will be obvious that some standard universal method of determination of moisture in flour is required; in the meantime all statements of percentage moisture in wheats or flours should be accompanied by a statement of the exact conditions under which the test was carried out.

CHAPTER III

ACIDS, BASES AND SALTS

ACIDS

THE name "oxygene," meaning acid-former, was given by the great French chemist Lavoisier to the gas which was found to be the active constituent of the atmosphere.

He so called it because he found that when certain common elements like phosphorus, sulphur, and carbon were burnt in it they produced substances which with water formed bodies which were acidic in nature, i.e. they had the characteristic property of changing the colour of certain vegetable substances called *indicators*. Thus:

(1) Phosphorus forms phosphoric acid:

$$4P + 5O_2 = \underset{\text{phosphorus pentoxide}}{2P_2O_5}$$

$$P_2O_5 + 3H_2O = \underset{\text{phosphoric acid}}{2H_3PO_4}$$

(2) Carbon forms carbonic acid:

$$C + O_2 = CO_2$$
$$CO_2 + H_2O = \underset{\text{carbonic acid}}{H_2CO_3}$$

(3) Sulphur forms sulphurous acid:

$$S + O_2 = SO_2$$
$$SO_2 + H_2O = \underset{\text{sulphurous acid}}{H_2SO_3}$$

All non-metals which combine with oxygen give oxides which are acidic, i.e. with water form acids.

Acids have the following characteristic properties :

(1) They are usually sour, corrosive, poisonous substances, soluble in water, e.g. the three mineral acids.* Sulphuric acid H_2SO_4, nitric acid HNO_3, and hydrochloric acid HCl are all corrosive and when dissolved in much water have a sour taste.

(2) They usually have the power of changing the colour of certain colouring matters called indicators, e.g. acids change the colour of litmus from blue to red.

(3) The most important property of acids is that they all contain the element hydrogen, part or all of which is replaceable by metals with the formation of *salts*. The actual replacement of the hydrogen can be carried out by a variety of methods which will be considered under the heading "Salts."

Sulphuric Acid, H_2SO_4, Oil of Vitriol. This is a substance of extreme commercial importance, many thousands of tons being produced annually. It is usually prepared from sulphur or some sulphur-bearing minerals which on combustion yield sulphur dioxide. This substance is a gas which by interaction with air in the presence of a *catalyst* † combines with a further atom of oxygen, yielding sulphur trioxide. Sulphur trioxide on combination with water yields sulphuric acid :

$$S + O_2 \xrightarrow{\text{burning}} \underset{\text{sulphur dioxide}}{SO_2}; \qquad SO_2 + O \xrightarrow{\text{catalyst}} \underset{\text{sulphur trioxide}}{SO_3}$$

$$SO_3 + H_2O = \underset{\text{sulphuric acid}}{H_2SO_4}$$

Sulphuric acid is a thick oily liquid with a density of nearly two. It has a vigorous affinity for water, and much heat is evolved when the acid is poured into water. The concentrated acid will also abstract the elements of water from many vegetable and animal substances, often leaving just a mass of carbon ; thus it chars immediately cloth, paper, wood, and the like. The diluted acid is by no means so violent in its action. The diluted acid dissolves certain metals, yielding

* So called because they are prepared from minerals : sulphuric acid from sulphur, nitric acid from nitre, and hydrochloric acid from common salt.

† Catalyst is a body which accelerates the rate of chemical interaction without itself undergoing any obvious change.

hydrogen and a salt of the acid, i.e. the metal takes the place of hydrogen in the acid, e.g. :

$$H_2SO_4 + Zn = ZnSO_4 + H_2$$

Similar reactions occur with iron and magnesium.

The salts produced are called " sulphates." Traces of the sulphates of calcium and magnesium are often to be found in samples of " hard " water. Likewise, there are traces to be found in the " ash " from wheat and flour.

Hydrochloric Acid, HCl, Spirit of Salt. This acid is obtained from common salt by heating it with sulphuric acid :

$$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4$$

Formerly the hydrochloric acid was employed to prepare chlorine, but with modern methods chlorine is first obtained by the electrolysis of common salt and this is burnt with hydrogen to form hydrochloric acid :

$$H_2 + Cl_2 = 2HCl$$

Hydrochloric acid or hydrogen chloride is a gas which fumes in air and is extremely soluble in water forming the so-called hydrochloric acid. This solution has all the properties of an acid, dissolves metals, and forms salts called chlorides. Common salt is the chloride of sodium, NaCl.

Nitric Acid, HNO_3, Aqua Fortis. Prepared by the older method, by heating sodium nitrate (Chile saltpetre) with sulphuric acid :

$$2NaNO_3 + H_2SO_4 = 2HNO_3 + Na_2SO_4$$

Of recent years nitric acid has been successfully produced on a commercial scale by an electrical method from air. This process will be sketched briefly under nitric oxide. The production of nitric acid from the atmosphere is gradually displacing the older method of manufacture from Chile saltpetre.

Nitric acid is a colourless, extremely corrosive liquid. The concentrated acid dissolves many metals, yielding oxides of nitrogen and a nitrate of the metal. The acid is employed largely in the production of explosives and for the manufacture of nitrates which are employed as artificial fertilisers to replenish the soil with fixed nitrogen.

Other acids which are of interest to the student of Flour Milling are :

Phosphoric Acid, H_3PO_4. This is a solid acid made from "bone ash," * which consists largely of the calcium salt of phosphoric acid, $Ca_3(PO_4)_2$.

The finely crushed material is treated with a definite quantity of diluted sulphuric acid, and insoluble calcium sulphate is precipitated and phosphoric acid remains in solution and may be obtained by evaporation of the water :

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$$

A weak solution of phosphoric acid is sometimes sprayed on to flour stocks to improve the quality of the flour.

Calcium phosphate, $Ca_3(PO_4)_2$, is one of the most important salts of phosphoric acid. It occurs naturally in rocks, mineral phosphates and bones. Vegetable life require phosphorus in the form of phosphates for proper nutrition. These are normally forthcoming by the disintegration of rocks, etc., and the calcium phosphate is slowly distributed in the soil by dissolving in small quantities in water and thus rendered available for plants.

To replenish soil exhausted of phosphates by the growth of crops, it is usual to apply artificial fertilisers. Calcium phosphate from bones is converted to a more soluble acid phosphate by the addition of the regulated quantity of sulphuric acid :

$$Ca_3(PO_4)_2 + 2H_2SO_4 = \underset{\text{acid calcium phosphate}}{Ca(H_2PO_4)_2} + 2CaSO_4$$

The mixture of acid calcium phosphate and calcium sulphate is termed "superphosphate," and is employed as an artificial fertiliser.

Phosphates absorbed by plants appear eventually in what is termed the mineral matter or *ash*.† Thus the ash of most cereals consists largely of the phosphates of potassium, calcium, and magnesium. These mineral salts of wheat differ with the varieties and soils on which they are grown, but on

* "Bone ash" is the residue left when clean bones have been heated in the presence of air. By this heating the whole of the "organic" or "non-mineral" matter of the bones is burnt away and the residue is termed the "ash."

† The "ash" of a substance is the residue remaining when the substance is strongly heated in air. It consists of the "inorganic" or mineral constituents of the original substance, whilst the constituents burnt away are the "organic" or "non-mineral" constituents.

an average the ash from wheat contains approximately 75 to 80 per cent of acid potassium phosphate, KH_2PO_4, and magnesium phosphate, $Mg_3(PO_4)_2$.

It has been suggested that the " strength " of a sample of wheat or flour, i.e. its ability to produce a bold well-risen loaf, is connected with the presence of soluble phosphates in the wheat. Acid calcium phosphate is also used as an improver in flour, i.e. it improves the baking quality of the flour. It is also employed as the acid agent in baking powders. (See page 61.)

Tartaric Acid, $H_2(C_4H_4O_6)$. A solid organic acid occurring in grapes. The acid potassium salt of this acid, $KH(C_4H_4O_6)$, is called cream of tartar, and is used as the acid agent in baking powders.

During the manufacture of wine by the fermentation of grape juice, crude cream of tartar separates out from the liquor as a crust. This crude cream of tartar (termed " argol ") is the source from which tartaric acid is manufactured commercially.

Hydrogen Cyanide, HCN. This acid is one of the most deadly poisons known and is employed commercially for fumigating buildings where vermin, rats, etc., are liable to congregate and breed, e.g. in ships and in flour mills. When the fumigation operation is to be carried out, all windows and doors are closed and made gas-tight ; after it has been definitely ascertained that all persons have left the building, gaseous hydrogen cyanide is allowed to escape from a cylinder. After a period of twenty-four hours has elapsed, the doors, etc., are opened but no one is allowed to enter until a suitable period is allowed for ventilation and the air is declared safe to breathe. Hydrogen cyanide is made by distilling powdered potassium cyanide (KCN) with diluted sulphuric acid. The gaseous hydrogen cyanide is condensed to a liquid in a freezing mixture. The liquid boils at 26·5° C. and freezes to a white solid at −15° C.

An aqueous solution of the substance, termed " hydrocyanic acid," has a smell of bitter almonds and has all the common properties of acids. A 10 per cent aqueous solution is termed " prussic acid." Hydrocyanic acid is a weak monobasic acid and gives rise to salts, " cyanides," in the usual manner.

BASES

Whilst the non-metallic elements yield oxides which are acidic in character, metals give oxides which are in some ways the opposite in character to the acids and are called bases or basic oxides. These oxides form the " basis " of all salts. Thus magnesium oxide, MgO ; potassium oxide, K_2O ; and calcium oxide, CaO, are bases. They combine directly with acid oxides to form salts. Thus :

Base		*Acid Oxide*		*Salt*
MgO	+	CO_2	=	$MgCO_3$
magnesium oxide		carbon dioxide		magnesium carbonate

K_2O	+	SO_3	=	K_2SO_4
potassium oxide		sulphur trioxide		potassium sulphate

$3K_2O$	+	P_2O_5	=	$2K_3PO_4$
potassium oxide		phosphorus pentoxide		potassium phosphate

The characteristic properties of bases are as follows :

(1) They react with acids forming salts and water. As a result of this interaction, part or all of the hydrogen of the acid may be replaced by a metal. If *all* the hydrogen is replaced, the product is termed a *normal* salt. Thus :

Base		*Acid*		*Normal Salt*		
MgO	+	H_2SO_4	=	$MgSO_4$	+	H_2O
magnesium oxide		sulphuric acid		magnesium sulphate		water

If only part of the hydrogen of the acid is replaced the product is termed an *acid* salt, though the term is rather misleading ; e.g. :

Base		*Acid*		*Acid Salt*		
K_2O	+	$2H_2SO_4$	=	$2KHSO_4$	+	H_2O
potassium oxide		sulphuric acid		potassium hydrogen sulphate		water

(2) Many bases unite with water forming *hydroxides* (i.e. oxide + water), e.g. :

Na_2O	+	H_2O	=	$2NaOH$
sodium oxide				sodium hydroxide or caustic soda

CaO	+	H_2O	=	$Ca(OH)_2$
calcium oxide or quick lime				calcium hydroxide or slaked lime

In many cases the hydroxides so produced are soluble in water, and the solution colours red litmus blue. Such substances are termed *alkalies* and they have very much the same properties as the bases, i.e. they react with acids forming salts and water, e.g. :

Alkali		*Acid*		*Salt*		*Water*
$NaOH$	+	HCl	=	$NaCl$	+	H_2O

Common alkalies are $NaOH$, caustic soda or sodium hydroxide; $Mg(OH)_2$, magnesia or magnesium hydroxide; KOH, caustic potash or potassium hydroxide; $Ca(OH)_2$, slaked lime or calcium hydroxide.

SALTS

Salts are bodies produced by the interaction of a base (or an alkali) with an acid.

The chief classes* of salts are :

(1) Normal salts produced by replacing all the hydrogen of an acid by a metal, e.g. $NaCl$, K_3PO_4.

(2) So-called " acid salts " produced by the replacement of part of the hydrogen of an acid by a metal, e.g. $KHSO_4$, potassium hydrogen sulphate.

The term " acid salt," used to describe this class of salt, is rather misleading, for although some so-called acid salts react acid to indicators, many do not. The behaviour with indicators is dependent on the nature of the acid and base used to form the salt.

As a rule, salts produced from *strong* bases and *strong* acids behave in the normal fashion, i.e. their normal salts react neutral and their acid salts, acid to indicators.

A strong base may be described as one with a vigorous chemical affinity for an acid and vice versa for a strong acid ; e.g. $NaOH$ (caustic soda) and H_2SO_4 (sulphuric acid) have a vigorous affinity for each other and are described as a strong base and strong acid respectively.

When two molecules of caustic soda interact with one molecule of sulphuric acid, the product, normal sodium sulphate, is neutral to indicators and is quite stable and unaffected by water :

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$

The process is termed a *neutralisation.*

* A third class, " basic salts," will not be considered here.

When only one molecule of caustic soda is employed, however, only one hydrogen atom of the acid is replaced by sodium, and the product $NaHSO_4$, sodium hydrogen sulphate, since it still contains a hydrogen atom of the original acid, reacts acid to indicators :

$$NaOH + H_2SO_4 = NaHSO_4 + H_2O$$

Moreover, sodium hydrogen sulphate is quite stable and unaffected by water.

In the two salts considered the base and the acid are firmly united. When, however, salts produced from either a weak base or a weak acid are considered, it is found that they do not behave normally to indicators, e.g. $NaHCO_3$, sodium bicarbonate, reacts alkaline to indicators, so also does Na_2CO_3, sodium carbonate, although the former should be an acid salt and the latter a normal or neutral one.

These two salts are produced from a strong base and a weak acid, carbonic acid, whose chemical affinity for each other is not sufficiently great to enable the salts to resist a partial decomposition by water.

This partial decomposition by water, termed *hydrolysis*, results in the re-formation of some of the original base and acid. The effect of the presence of the strong base and weak acid is to cause the solution to react alkaline to indicators.

As a matter of fact this hydrolysis occurs with nearly all salts, except those of the strongest acids and bases.

Those acid salts which behave normally react as mild acids, e.g. $Ca(H_2PO_4)_2$, acid calcium phosphate ; $KH(C_4H_4O_6)$, potassium hydrogen tartrate. These two substances may be employed as the acid agent in baking powders to generate carbon dioxide from the admixed sodium bicarbonate.

Acid calcium phosphate and acid potassium phosphate are also employed as improving agents in flour. They are said to increase the acidity of the dough in bread-making, a feature reputed to have a beneficial effect on the gluten.

The actual replacement (partly or wholly) of the hydrogen of an acid may be carried out in a variety of ways :

(1) By direct interaction with a metal, e.g. :

$$Mg + H_2SO_4 = MgSO_4 + H_2$$

(2) By neutralisation with a base, e.g. :

$$CaO + 2HCl = CaCl_2 + H_2O$$

(3) By interaction with an alkali, e.g. :

$$KOH + H_3PO_4 = KH_2PO_4 + H_2O$$

(4) By interaction with a carbonate or bicarbonate, e.g. :

$$Na_2CO_3 + H_2SO_4 = H_2O + CO_2 + Na_2SO_4$$

$$NaHCO_3 + KH(C_4H_4O_6) = NaK(C_4H_4O_6) + CO_2 + H_2O$$

Notice that in each case, as the reagent used for causing the replacement varies, the products, additional to the salt formed, vary. It may be noticed from some of the equations given that the replacing power of the elements differs. One atom of sodium takes the place of one atom of hydrogen only, whereas one atom of calcium or magnesium can take the place of two atoms of hydrogen.

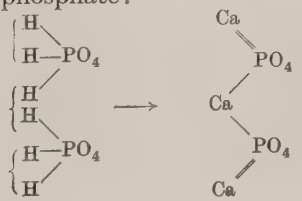
This number, which expresses the *number of atoms of hydrogen which will combine with or take the place of one atom of another element*, is called its " hydrogen combining power " or *valency*.

Thus among the mono- or one-valent elements are chlorine, sodium, potassium (e.g. HCl, NaCl, KCl), whilst oxygen, sulphur, calcium, magnesium, have a valency of two and are di-valent (e.g. H_2O, H_2S, CaO, MgO).

Some elements can exhibit more than one valency and combine with other elements in more than one proportion, e.g. sulphur exhibits valencies of two in sulphuretted hydrogen, H_2S ; four in sulphur dioxide, SO_2 : and six in sulphur trioxide, SO_3. Nitrogen has valency of three in ammonia, NH_3, and five in nitric acid and nitrates.

The valency of an element helps us to remember the formula of a salt provided the formula for the corresponding acid be known ; e.g. :

normal calcium phosphate, the valency of calcium is two, the formula of phosphoric acid is H_3PO_4. To replace hydrogen completely in phosphoric acid we need six hydrogen atoms, taken two at a time ; this gives us $Ca_3(PO_4)_2$ as the formula for calcium phosphate:



CHAPTER IV

NITROGEN—AMMONIA—OXIDES OF NITROGEN—CHLORINE

NITROGEN

THE element nitrogen occurs free in abundance in the atmosphere surrounding the earth. Approximately 80 per cent of the gases constituting air is the element nitrogen. The remainder consists of oxygen and traces of carbon dioxide, water vapour, and other gases.

Nitrogen also occurs in the combined form as nitrates, ammonium compounds in the inorganic world, and as various complex compounds in the organic or animal and vegetable world, e.g. proteins. It is present in the gluten of wheat.

The element nitrogen, when free, is a relatively inert and unreactive element. It is the inactive constituent of the atmosphere, left behind when substances burn and use up the oxygen in the air. It is in the combined form as a nitrate or an ammonium compound that it is a reactive or a useful element.

Nitrogen combines directly only with difficulty with other elements, e.g. oxygen to give oxides of nitrogen, or hydrogen to give ammonia, both of which methods are employed commercially for the fixation of atmospheric nitrogen for the production of reactive or useful compounds.

To obtain nitrogen from the atmosphere, air is liquefied and then advantage taken of the fact that the nitrogen boils off first when the liquid air is allowed to boil. The nitrogen is pumped away and compressed in cylinders. The oxygen, which boils off last, is similarly treated. Liquid nitrogen boils at $-196°$ C., liquid oxygen at $-182°$ C.

Ammonia, NH_3 (hydrogen compound of nitrogen). The importance of ammonia and its compounds will be gathered from the section dealing with the assimilation of nitrogen compounds from the air and the soil (page 47). All the nitrogen in the universe passes through a cycle of change, of which nitrogen in the form of ammonia is one stage.

Most of the ammonia of commerce is derived from one of two sources :

(1) The distillation of coal.
(2) The nitrogen of the atmosphere, by union with hydrogen (synthetic production).

(1) Coal contains as one of its constituent elements, nitrogen, present in the original vegetable matter from which the coal is formed. When coal is distilled in the absence of air during the manufacture of coal gas, some of the nitrogen present is converted to ammonia and appears in the gas-works products as "ammoniacal liquor." This liquor is an aqueous solution containing ammonia and its salts. By treatment with lime and heating, the ammonia is liberated in gaseous form and is either absorbed in water to form "liquid" ammonia (really an aqueous solution) or in sulphuric acid to form ammonium sulphate, a crystalline substance employed in its crude state as an artificial fertiliser and after refining as one of the component parts of a flour improver.

The equations for the production of gaseous ammonia from ammonium salts in ammoniacal liquor and its absorption in water or sulphuric acid are as follows:

$$\underset{\text{present in liquor}}{(NH_4)_2SO_4} + \underset{\text{slaked lime}}{Ca(OH)_2} = CaSO_4 + 2H_2O + 2NH_3$$

$$NH_3 + H_2O = \underset{\text{ammonium hydroxide}}{NH_4OH}$$

$$2NH_3 + H_2SO_4 = \underset{\text{ammonium sulphate}}{(NH_4)_2SO_4}$$

(2) Ammonia is now produced on a commercial scale by the Haber Process, whereby hydrogen (from electrolysis of water) and nitrogen (from the air) are caused to unite at high temperature and pressure in the presence of a *catalyst*:

$$N_2 + 3H_2 = 2NH_3$$

Ammonia is now produced in this country by this method.

PROPERTIES OF AMMONIA.

(1) It is a colourless *gas* with a pungent odour and is readily liquefied at 10° C. and 6–7 atmospheres pressure. When the liquid evaporates it absorbs a considerable amount of heat, and the temperature of the surroundings may drop below 0° C., a fact employed in refrigerating machines for production of ice.

(2) It is readily soluble in water; 1 volume of water at 0° C. dissolves 1,298 volumes of ammonia, which can be all expelled by boiling. The strongest solution obtainable at room temperature has the density ·880 and contains 35 per cent NH_3. The solution so produced turns red litmus blue and has all the properties of an alkali hydroxide.

It is presumed therefore that combination takes place between the ammonia and the water, thus :

$$NH_3 + H_2O = NH_4OH$$

ammonium hydroxide

The (NH_4) group of elements behaves like a single element and is called the *ammonium radical.*

Thus, like NaOH, sodium hydroxide, it neutralises HCl, hydrochloric acid, to form ammonium chloride (sal-ammoniac) and water :

$$NH_4OH + HCl = NH_4Cl + H_2O$$

cf. $$NaOH + HCl = NaCl + H_2O$$

Compare the two series of compounds :

NaOH	NH_4OH	hydroxide
NaCl	NH_4Cl	chloride
$NaNO_3$	NH_4NO_3	nitrate
Na_2CO_3	$(NH_4)_2CO_3$	carbonate

All ammonium salts, on heating with an alkali (slaked lime, $Ca(OH)_2$, or caustic soda, NaOH), liberate gaseous ammonia :

$$(NH_4)_2SO_4 + Ca(OH)_2 = CaSO_4 + 2NH_3 + 2H_2O$$

$$NH_4Cl + NaOH = NaCl + H_2O + NH_3$$

The Oxides of Nitrogen. It has been stated previously that an oxide is a compound of an element with oxygen.

The element nitrogen has the ability of combining with oxygen in more than one proportion to produce five different oxides, only two, however, of which need be considered in connection with flour milling. These five oxides of nitrogen are as follows :

(1) N_2O, nitrogen monoxide or nitrous oxide ("Laughing Gas").
(2) N_2O_2 or NO, nitrogen dioxide or nitric oxide,
(3) N_2O_3, nitrogen trioxide, the anhydride of nitrous acid, for with water it yields the unstable nitrous acid.

(4) N_2O_4 or NO_2, nitrogen tetroxide or nitrogen peroxide.
(5) N_2O_5, nitrogen pentoxide, the anhydride of nitric acid, for with water it yields nitric acid.

Nitric Oxide or Nitrogen Dioxide, NO. This is an important oxide of nitrogen from many points of view. For laboratory purposes it may be prepared by the following method:

By treating copper with nitric acid (density 1·2) and purifying the NO so produced from other nitrogen oxides by absorption in ferrous sulphate solution at below 25° C. and subsequently heating this. The gas so liberated will contain about 99 per cent NO.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$$

$$2FeSO_4 + NO \underset{\text{below } 25^\circ}{\overset{60^\circ}{\rightleftharpoons}} 2FeSO_4.NO$$

dark brown substance

On a commercial scale nitric oxide is an exceedingly important substance. Its production from nitrogen and oxygen of the air under the influence of an electric discharge forms the first stage in the "Fixation of Atmospheric Nitrogen" in the manufacture of nitric acid and nitrates. The same method is employed to produce nitric oxide to form nitrogen peroxide for the bleaching of flour.

The synthetic production of nitric acid and nitrates is sufficiently important to devote a short space to it.

Nitrogen, in the free state, is abundant in the atmosphere, but is a relatively inert element. Yet this element plays an essential part in vegetable and animal metabolism, and is an indispensable component of all foodstuffs. But for most plants the nitrogen, to be of any use, must be presented in a soluble combined form, e.g. as a nitrate or ammonium compound. These substances, along with others, the plants assimilate from the soil during their growth and build up into complex nitrogenous compounds which are called *proteins*. These proteins are one of the essential parts of the food of the human race.

Replenishment of the soil with the nitrogen compounds used up was accomplished to some extent naturally, thus:

(1) By the formation of nitric acid in small quantity by atmospheric electrical discharge, the acid becoming neutral-

ised to form nitrates which were washed into the soil. About 11 lbs. of nitrate per acre annually are produced in this way.

(2) Certain micro-organisms are to be found on the roots of leguminous plants and enable them to assimilate free nitrogen, e.g. on the roots of peas and beans.

(3) By the decomposition of waste animal products ; these contain nitrogen in the form of urea, which slowly decomposes in the soil through the agency of certain " nitrifying " bacteria, producing first ammonium compounds and finally nitrates.

Under conditions of artificial cultivation, process (3) causes a loss of nitrogen since it is often diverted to the sea, and it becomes necessary to supply nitrogenous fertilisers, such as ammonium sulphate (from the distillation of coal) or sodium nitrate. It is further necessary to supply artificial fertilisers by reason of reduction of fertility of the soil due to the continuous and heavier cropping carried out under modern conditions.

Most of the sodium nitrate in the past, required for this purpose, was obtained from the Chile saltpetre beds, enormous deposits of salts, consisting largely of sodium nitrate, which are to be found over a wide area in the rainless regions to the west of the Andes mountains in South America. These deposits are being used up at a rapid rate, and there is the possibility that some day supplies will be exhausted. During the late European war the question of supplies of sodium nitrate from Chile (for manufacturing nitric acid for explosives) became acute for the enemy countries, and it was largely owing to this acuteness that methods were developed for manufacturing nitric acid without the use of sodium nitrate, namely from the air, by the " Fixation of the Atmospheric Nitrogen." The basis of this process is the union of nitrogen and oxygen, forming nitric oxide, NO, under the influence of a high tension electrical discharge. The process can best be worked on a large scale economically in the neighbourhood of cheap water power, e.g. in Norway and Niagara Falls, the water power producing cheap electrical power. The actual process of manufacture is to blow a rapid current of air through an electric arc which, by various devices, is spread out into a sheet of flame. At the high temperature of the arc (about 3,000° C.) *some* oxygen and nitrogen unite to form nitric oxide. The exit gases from the furnaces contain usually

about 1·5 per cent of nitric oxide. The air is blown rapidly through the arc and cooled down rapidly in order to preserve as much nitric oxide as possible, it being unstable above 1,200°. The gases containing the nitric oxide then pass to an oxidation chamber where, at a much lower * temperature (below 600°), nitric oxide combines with more oxygen to form NO_2, nitrogen peroxide.

Up to this point the procedure for making NO_2 on a commercial scale and its preparation for the bleaching of flour are the same. But at this point in the bleaching of flour, air containing a small, known amount of NO_2 is passed into an agitator and mixes with the flour to be bleached. Whilst for the production of nitric acid or nitrates, the gases containing NO_2 pass to absorption towers where the NO_2 is absorbed, either by water or alkalies :

$$2NO_2 + H_2O = HNO_3 + HNO_2$$

followed by

$$3HNO_2 = HNO_3 + H_2O + 2NO$$

(passes back for further absorption)

The nitric acid produced may be further concentrated by distillation with sulphuric acid or neutralised by lime to give calcium nitrate which is sold as a fertiliser under the name "Norwegian Saltpetre."

The Bleaching of Flour by Nitrogen Peroxide. Bleaching of flour was first carried out by a process, due to Andrews, by which the nitrogen peroxide was produced by chemical means. Later it was made electrically by the Alsop Process (1904). This process employed a flaming arc through which air was blown. The arc was obtained from two electrodes, one fixed and the other moving to and fro above it, causing a make and break in the arc. The high temperature of the arc oxidised the nitrogen to nitric oxide, which in turn was oxidised to the peroxide and swept out of the apparatus by incoming air. Many modifications of the original process have been devised, but the principle is the same, the modification consisting in the mode of producing the flaming arc. It is stated that gases leaving the apparatus contain usually about 300–500 parts of NO_2 per million parts of air. These

* It is important to note the necessity for this cooling, since above 600° the reaction $NO + O \rightarrow NO_2$ is reversed. Also the reaction given is not complete until a much lower temperature is reached.

gases are mixed with air in a container so as to produce a gas mixture of uniform composition which is then blown into the horizontal agitator where it mixes with the flour. Vigorous agitation is essential for uniform bleaching ; or alternatively a vertical vessel may be employed and the flour falls in a shower and meets the rising stream of air containing the nitrogen peroxide.

PROPERTIES OF NITRIC OXIDE.

(1) Colourless gas which is slightly heavier than air.

(2) Very sparingly soluble in cold water.

(3) Brought in contact with air or oxygen below temperatures of 600° C. brown fumes of nitrogen peroxide (NO_2) are immediately produced :

$$2NO + O_2 = 2NO_2$$

This property is characteristic of nitric oxide and enables it to be identified.

(4) Soluble in ferrous sulphate solution, forming a dark brown compound which probably has the formula $2FeSO_4.NO$. This is an unstable compound which decomposes on heating, yielding pure nitric oxide.

(5) The gas is not combustible, and only supports combustion under special conditions.

(6) If mixed with hydrogen and passed over heated finely divided nickel, the gas is reduced to ammonia :

$$2NO + 5H_2 = 2H_2O + 2NH_3$$

This is the converse of the mechanism which takes place in the so-called " exothermic " process for the production of nitric oxide by the oxidation of ammonia—a method sometimes employed in the flour mill for producing nitric oxide. This method is also employed commercially in this country for the production of " synthetic nitrates " :

$$4NH_3 + 5O_2 = 4NO + 6H_2O + 215{,}000 \text{ calories } *$$

This reaction is termed an " exothermic " reaction because heat is liberated when it takes place. (*Ex* = out, *thermos* = heat.)

Nitrogen peroxide is produced by this method for flour bleaching in the following manner. The oxidation of ammonia to nitric oxide takes place only extremely slowly, even at

* See Chapter VII, p. 79.

elevated temperatures. It is found, however, that in the presence of the metal platinum, the *rate* at which the reaction proceeds is enormously increased. The platinum acts as a kind of stimulant to the reacting gases and is termed a *catalyst*. The ammonia is obtained from cylinders, and the quantity required regulated by adjustment of the pressure valve on the cylinder. After mixing in the requisite proportion with air,* the mixed gases are passed through a chamber containing the heated catalyst. To commence operations the platinum wire catalyst is heated to about 650°–700° C., but once the gases are passed over it and the reaction commences, sufficient heat is evolved from the reaction to keep the catalyst aglow. In fact, an observation window is usually provided in the reaction chamber so that the operator may see the platinum glowing and thereby be assured that the process is working correctly. The gases leaving the reaction chamber and containing the nitric oxide are passed through heat exchangers and cooled down to below 140°, when steam from the reaction condenses and the nitric oxide is converted to nitrogen peroxide. After further cooling down to room temperature and admixture with more air, if necessary, the gases finally pass to the agitator where they mix with the flour to be bleached.

The nitrogen peroxide probably bleaches by reason of some reaction with the moisture present in flour, such as

$$H_2O + 2NO_2 = \underset{\text{nitrous acid}}{2HNO_2} + O$$

The oxygen being produced in the "atomic" or active condition oxidises the colouring matter present to a colourless oxidation compound. Whatever mechanism occurs, a flour bleached by nitrogen peroxide contains, when freshly bleached, small detectable traces of nitrites. These have been produced by the interaction of the nitrous acid and some of the bases present in the flour. Nitrites are salts of nitrous acid, e.g. $NaNO_2$, sodium nitrite ; $(NH_4)NO_2$, ammonium nitrite.

CHLORINE

Chlorine—symbol, Cl ; atomic weight, 35·5—is a member of a natural group of elements designated the *halogens*. This

* Usually about 10–11 per cent NH_3 by volume.

word signifies "salt former," a name applied to them by Berzelius (a Swedish chemist), to indicate their ability to form salts just like common salt. The other members of the group are fluorine, bromine, and iodine. Chlorine does not occur naturally in the free state owing to its great chemical activity, but it is to be found abundantly combined with other elements, chiefly as chlorides. These are found :

(1) In solution in sea water. Of the 3 per cent of solids usually found in an average sample of sea water, by far the greater proportion is sodium chloride, common salt.

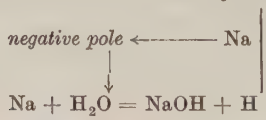
(2) As a mineral, rock salt, in various parts of the world, e.g. Cheshire.

(3) In the Stassfurt * deposits as a mineral called potassium chloride and as magnesium chloride.

The common salt of commerce is obtained either by mining the rock salt (as with coal), and then purifying it by process of recrystallisation, or by dissolving out the salt with water from its bed in the mine and pumping the solution to the surface where it is purified. Common salt and perhaps potassium chloride are the two main sources from which the element chlorine is obtained.

PRODUCTION OF CHLORINE.

Most of the chlorine used in commerce to-day is a by-product from the electrolytic production of caustic soda from aqueous solutions of common salt, or from electrolytic production of sodium from fused sodium chloride. When an electric current is passed through a brine solution in a suitable cell, the sodium chloride is decomposed and chlorine is liberated at the positive pole or anode, whilst at the negative pole or cathode the liberated sodium reacts with the water, forming caustic soda and hydrogen :



Precautions need to be taken to ensure that the reactive chlorine does not interact with the sodium hydroxide (caustic soda) produced. The chlorine is pumped away, compressed,

* Germany.

liquefied, and stored in steel cylinders. Liquid chlorine is now a fairly common article of commerce, and has a wide range of uses, one of which is to mix in gaseous form with air as a maturing and bleaching agent for flour.

PROPERTIES OF CHLORINE.

(1) Chlorine is a greenish-yellow gas, heavier than air (density at $0° = 2{\cdot}49$, air $= 1$).

(2) Liquid chlorine boils at $-33{\cdot}6°$ C. at 760 mm. pressure, and solidifies to a crystalline mass at $-102°$ C.

(3) It has a suffocating smell and attacks the membranes of the eyes, nose, throat, and produces coughing and great discomfort. If inhaled in large quantities it produces permanent harm to the lungs.

Chlorine is not poisonous (as is hydrogen cyanide), its harmful effect being chiefly due to its irritant properties. For small inhalations, relief may be secured by drinking milk.

Chlorine is an extremely reactive element. It combines very readily with most other elements, e.g. hydrogen, sodium, etc., to give chlorides. Iron is not attacked by the gas in absence of water at ordinary temperatures. Chlorine is soluble in water, to give a green solution smelling of chlorine, and termed "chlorine water." This, however, is unstable and decomposes slowly, the chlorine uniting with the hydrogen of the water and liberating the oxygen. This demonstrates the remarkable affinity that chlorine has for hydrogen.

$$Cl_2 + H_2O = 2HCl + O$$

This change is the key to the reactivity of chlorine in bleaching, for the oxygen liberated is in the *atomic* or *nascent* condition, which is extremely reactive. The usually accepted explanation of the bleaching of colouring matters by chlorine is as follows:

The colouring matter is oxidised by the atomic oxygen, forming a colourless oxidation compound.

Some support for this explanation is to be obtained from the fact that chlorine has no bleaching effect in the absence of water. Chlorine will readily bleach writing ink, Turkey red cloth, etc., if water be present but not in absence of water. Perfectly dry chlorine does not bleach any colouring matter, indicating that water must play an essential part in the change. Probably this change is one of those which takes place in the bleaching of flour.

USES OF CHLORINE.

(1) Preparation of bleaching powder for bleaching of paper, cotton goods, etc.

(2) Preparation of many chlorides used industrially.

(3) Preparation of intermediate compounds in manufacture of dyestuffs.

(4) Sterilisation of drinking water (it kills bacteria), and disinfection of sewage, etc.

(5) Maturing and bleaching of flour.

CHAPTER V

CARBON—FUELS—OXIDES OF CARBON—AERATING AGENTS

Carbon is a solid element which occurs naturally on the earth's surface in a number of different physical forms. In the free state it is present to a large extent in *coal*. Coal represents the final product in the decay of vegetable tissue. This decay, which takes place over centuries, occurs in such a way that most of the hydrogen and oxygen of the original vegetable matter is lost, leaving largely carbon. From coal during the manufacture of coal gas, *coke* is obtained, and coke is very largely carbon.

Graphite is another form of carbon which is to be found naturally, though much of it to-day is prepared artificially from other forms of carbon. Graphite is used largely as a lubricating agent.

The *diamond* is a form of carbon. It is a relatively simple matter to convert a diamond to ordinary carbon by heating it to a high temperature, though it is by no means easy to convert ordinary carbon to a diamond. Both the diamond and ordinary carbon are composed of the same kind of matter but in different physical forms.

In addition to these carbon can be prepared in several other forms :

(1) As *soot* by partially burning substances rich in carbon such as turpentine, acetylene.

(2) As *wood charcoal*, or *bone charcoal* by heating wood or

bones in the absence of air. Sundry gases and volatile liquids are lost, and charcoal is left behind.

(3) The purest form of carbon obtainable is prepared from sugar. Sugar contains the elements carbon, hydrogen, and oxygen.

On removing the hydrogen and oxygen in the form of water by heating with concentrated sulphuric acid, a black mass of sugar carbon is left.

PROPERTIES OF CARBON.

Considering only the non-crystalline varieties of carbon, i.e. charcoal, soot, coke, etc., the physical constants of these vary only slightly, e.g. the density varies between 1·4 to 1·7.

Charcoals have the power of absorbing large volumes of gases, hence their use in respirators.

On heating carbon it does not melt but burns readily in air or oxygen without smoke, forming carbon dioxide:

$$C + O_2 = CO_2$$

The temperature at which it commences to burn varies with the different varieties. When carbon unites with oxygen in this way to form carbon dioxide it produces a considerable quantity of heat. Now carbon, a fairly reactive chemical element, is possessed of a certain amount of chemical energy which on combustion is converted to another form, viz. thermal energy or heat. This thermal energy or heat is used for many domestic and industrial purposes, and most of our mechanical and electrical energy is derived from the combustion of carbon in the form of coal.

The calorific value or heating value of carbon is 8,080 calories per gm., i.e. when a gram of carbon is burnt completely to carbon dioxide, 8,080 calories of heat are liberated; 1 calorie of heat is the amount of heat required to raise the temperature of one gram of water by 1° C. Thus the complete burning of carbon can be represented:

$$C + O_2 = CO_2 + 96{,}960 \text{ calories (i.e. } 8{,}080 \times 12 \text{ cals.)}$$

The commercial value of coal, as indeed of any fuel, is determined by its calorific value. The calorific value of gaseous fuels is expressed as calories per cubic foot, and coal gas is now sold on a heating value basis. The gas companies are required by Parliament to charge for gas on the basis of its heating value, and to declare what that heating value is

from time to time; e.g. a sample of coal gas may be quoted as having a calorific value of 141,120 calories per cubic foot. More often the value is quoted in British Thermal Units per cubic foot, e.g. 560 British Thermal Units per cubic foot, where a British Thermal Unit (B.Th.U.) is the commercial unit of heat in this country, and is the amount of heat required to raise the temperature of 1 lb. of water through 1° F.

Not only does carbon, when heated, combine with oxygen present in the free state, but it will also sometimes unite with oxygen which is already combined, e.g. in oxides. This fact is employed industrially in obtaining metals from their ores. The ores are converted to oxides which are then heated with coke, thus liberating the metal and forming one of the oxides of carbon. In the manufacture of iron and steel, iron oxide is heated to a high temperature, mixed with coke, when the following change ensues:

$$\underset{\text{iron oxide}}{Fe_2O_3} + 3C = 2Fe + \underset{\text{carbon monoxide}}{3CO}$$

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2$$

Oxides of Carbon. Two oxides of carbon are known: carbon monoxide, CO, and carbon dioxide, CO_2. Thus it is seen that carbon is able to unite with oxygen in two different, but yet quite definite, proportions. Of these two oxides carbon dioxide is the most important to flour-milling students, and carbon monoxide will only be briefly considered.

Carbon monoxide, CO, is a gas produced by the partial combustion of carbon, or by the removal of part of the oxygen from carbon dioxide. Thus:

$$2C + O_2 = 2CO$$
$$CO_2 + C = 2CO$$

In carbon monoxide the carbon is unsatisfied with its quota of oxygen, and will readily take up more, forming the dioxide; e.g. it burns in air with a blue flame forming CO_2:

$$2CO + O_2 = 2CO_2$$

Carbon monoxide also *reduces* oxides of metals to the metallic state:

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2$$

It is used commercially as a fuel, being produced, mixed with hydrogen (another combustible), by the action of steam on red-hot coke:

$$H_2O + C = H_2 + CO$$

The resulting mixture of hydrogen and carbon monoxide is termed " water gas."

Carbon monoxide is extremely poisonous, and since it has no smell it is rather difficult to detect its presence. Coal gas contains a small percentage of carbon monoxide, and it is to this gas that the poisonous character of coal gas is due.

Carbon Dioxide, CO_2.

This gas occurs widely distributed in the universe, both in the free state and combined in the form of carbonates. It is to be found in the atmosphere, normally to the extent of ·03 per cent by volume. This amount varies with conditions, since the combustion of any carbonaceous matter, or the breathing of animals, tends to increase the quantity locally. A rough balance is maintained, however, by reason of the fact that plants assimilate carbon dioxide during their growth. The carbon dioxide combines with water in the plant under the influence of sunlight to form starch and other products. In the combined form carbon dioxide occurs abundantly in the form of carbonates, chiefly calcium carbonate, $CaCO_3$, found as marble, chalk, limestone, etc. Carbon dioxide is also produced by the fermentation of sugar by yeast. It is the gas given off in the fermentation of dough by yeast. For ordinary experimental purposes in the laboratory, carbon dioxide may be obtained by the action of dilute hydrochloric acid on calcium carbonate:

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

On a commercial scale carbon dioxide is obtained as a by-product as a result of fermentation in the brewing industry.

Physical Properties of Carbon Dioxide.

(1) It is colourless gas, heavier than air.

(2) A non-supporter of combustion, in fact it extinguishes flames and is used in fire extinguishers. If a jar of carbon dioxide be poured on to some burning benzene the flames are extinguished.

(3) It is not poisonous, though an atmosphere of carbon dioxide suffocates for lack of oxygen.

(4) Carbon dioxide liquefies at low temperature and increased pressure (e.g. at $-5°$ C. and 30·8 atmospheres pressure). If the liquid be allowed to evaporate, the latent heat required

is absorbed from the surroundings and the temperature falls. This principle is employed in refrigerating machinery.

Chemical Properties of Carbon Dioxide.

(1) With lime water, a turbidity is produced, due to the formation of finely divided insoluble calcium carbonate, according to the equation:

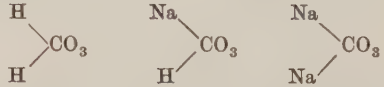
$$\underset{\text{present in lime water}}{Ca(OH)_2} + CO_2 = \underset{\text{insoluble}}{CaCO_3} + H_2O$$

This test is commonly employed in testing for the presence of carbon dioxide.

(2) Carbon dioxide is slightly soluble in water at the ordinary temperature and pressure. At normal temperature and pressure (0° C. and 760 mm. pressure) 1 c.c. of water will dissolve 1·7 c.c. CO_2. The solubility increases with increase in pressure, a factor employed in the manufacture of "soda water." Whilst the dry gas has no effect on indicators, e.g. litmus, the solution reddens litmus, indicating the presence of an acid presumably produced by the union of carbon dioxide and water. Thus:

$$CO_2 + H_2O = \underset{\text{carbonic acid}}{H_2CO_3}$$

This substance, presumed to exist in an aqueous solution of carbon dioxide, has never been isolated, but the solution nevertheless exhibits all the properties of an acid; e.g. it gives two salts by replacement of the hydrogen by a metal in two stages. Thus:



H_2CO_3	$NaHCO_3$	Na_2CO_3
carbonic acid	sodium bicarbonate	sodium carbonate (or soda)

Similarly carbonates and bicarbonates of other metals are known; e.g. $Ca(HCO_3)_2$. Calcium bicarbonate causes the temporary hardness of water.

All carbonates and bicarbonates on treatment with diluted acid liberate their carbon dioxide:

$$NaHCO_3 + HCl = NaCl + H_2O + CO_2$$
$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

All bicarbonates on heating alone decompose, liberating carbon dioxide, and leave a residue of the normal carbonate. Thus :

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$$
$$Ca(HCO_3)_2 = CaCO_3 + CO_2 + H_2O$$

Sodium bicarbonate is a white powdery substance, sparingly soluble in cold water and decomposed by boiling water as indicated above. It is employed in conjunction with an acid agent for liberating the carbon dioxide in baking powders and self-raising flours.

THE USE OF CARBON DIOXIDE IN BREAD-MAKING

Bread is a light porous mass made by mixing flour and water, salt and yeast into a dough, and allowing it to ferment, when the carbon dioxide produced causes the dough to rise, i.e. the production of small bubbles of gas inside the dough causes it to expand to three or four times its original volume. The mass is then fixed by heating in an oven, when expansion of the gas produces a further increase in volume, and the resulting light and " aerated " product is termed " bread." The methods of producing the carbon dioxide for the " aeration " may be divided into two classes :

(1) Natural Aeration.
(2) Artificial Aeration.

(1) *Natural Aeration.* This class contains only the time-honoured method of producing the carbon dioxide by the fermentation of sugar by the micro-organism known as *yeast.* Bread has been made by this method from time immemorial, and this method is still generally used to-day. Briefly the process is as follows : Definite quantities of flour, salt, yeast, and water are mixed together to form a homogeneous mass called " dough." The dough is then set aside in a warm place to prove, i.e. to allow the fermentation to proceed and to allow the yeast to act upon the sugars present or formed in the flour and form carbon dioxide. The mass expands, due to formation of gas in the mass ; after kneading, to distribute the gas evenly through the mass, the dough is weighed off into tins, set to rise a short while, and then baked in an oven. The nature and mechanism of the change which

takes place when sugar is fermented by yeast to form alcohol and carbon dioxide is dealt with in Part II.

(2) *Methods of artificially aerating bread.* In these processes the source of the carbon dioxide is almost always sodium bicarbonate ($NaHCO_3$). The gas is obtained from it, either by (*a*) using it alone, when the heat of the oven decomposes it, yielding carbon dioxide, or (*b*) by admixture with an acid or acid salt which, on the addition of water especially at slightly elevated temperatures, will liberate carbon dioxide.

(*a*) When sodium bicarbonate is used alone a definite small quantity of it is mixed with the flour and water and baked in the oven. The bicarbonate decomposes according to the equation :

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$$

and the carbon dioxide causes the mass to become more or less porous. The residue left behind, sodium carbonate, or common soda Na_2CO_3, has a characteristic taste. This method is employed for making such articles as " soda cake."

(*b*) Methods where an acid or acid salt is employed in conjunction with sodium bicarbonate. Some of the commoner methods employ either a solid acid or acid salt. These have the advantage of ease in handling, and also the reagents can be mixed in with the flour in bulk ; for, provided the materials remain dry, no interaction occurs between the bicarbonate and the acid agent. Thus potassium hydrogen tartrate (cream of tartar) is mixed in the dry state with sodium bicarbonate in the proportion of two parts of the former to one of the latter, the mixture being quite stable in the absence of moisture. Definite quantities of this mixture are added to flour and stirred with the necessary water. Some slight evolution of carbon dioxide occurs, but the main action does not take place till the mass is placed in the oven. This is due to the fact that cream of tartar has only a limited solubility in cold water, whereas its solubility is far greater in hot water. Solution in water is necessary in order to bring the acid into intimate contact with the bicarbonate :

$$\underset{\text{potassium hydrogen tartrate}}{KH(C_4H_4O_6)} + NaHCO_3 = \underset{\text{potassium sodium tartrate}}{KNa(C_4H_4O_6)} + H_2O + CO_2$$

The residue left in the baked article is sodium potassium tartrate in small quantity. This is quite harmless.

Of recent years the substance acid calcium phosphate has tended to displace cream of tartar as the acid agent, largely owing to its lower price. This acts in precisely the same way as cream of tartar, but of course leaves behind a phosphate as a residue in the baked article :

$$\underset{\text{acid calcium phosphate}}{Ca(H_2PO_4)_2} + 2NaHCO_3 = Ca(NaHPO_4)_2 + 2H_2O + 2CO_2$$

These last two mixtures mentioned, viz. (*a*) cream of tartar and sodium bicarbonate, (*b*) acid calcium phosphate and sodium bicarbonate are employed in various forms.

(i) As baking powder. This is a dry powder sold usually for domestic uses and consists usually of either (*a*) or (*b*) above, mixed with rice flour in order to keep the materials dry. This is necessary, since if the mixtures be kept for any length of time they absorb moisture from the air, slowly evolve carbon dioxide and set to a solid cake.

(ii) In self-raising flours. Here either mixture (*a*) or (*b*) is mixed in with the flour in bulk ; in the case of (*a*) at about the rate of one pound of mixture to 20 lbs. of flour. Some care has to be taken in the mixing in order to ensure that the mixture is thoroughly homogeneous, i.e. the aerating agent is uniformly distributed throughout the flour. Baking powders and artificial aerating powders are commonly employed for the baking of small articles, such as cakes, pastries. The bulk of bread is still made using yeast.

CHAPTER VI

PHYSICS—UNITS—DENSITY AND SPECIFIC GRAVITY

Physics is that branch of science which deals with the *measurement* of the fundamental properties of matter. We will deal, therefore, first with the *units* which are employed in scientific measurement, i.e. the units employed to measure length, volume, weight, etc., of a substance. A " unit " may be defined as something in terms of which we measure a property ; for we measure the length of a pipe in terms of the

" inch " unit or if the result be inconveniently large, in terms of a bigger unit, e.g. the foot or the yard.

There are many *systems* of units employed for particular purposes; for all accurate scientific purposes, the *metric system* is used. This is in common use for every purpose on the Continent but only for scientific purposes in this country. The metric system has the advantage of simplicity since it is a decimal system, i.e. the ratio between successive units is 10.

The units of length are derived from the *metre*. Originally the metre was the one-forty-millionth of the meridian of longitude passing through Paris. It is now defined as the distance between two points on a bar of platinum kept at 0° C. This bar is kept at Paris, and is termed the " standard " metre. Copies of it are kept in various parts of the globe. For convenience in use, the metre is divided into ten equal parts, each one called a decimetre (prefix, deci; Latin, *decem* = ten). Thus:

1 metre = 10 decimetres, and a decimetre is $\frac{1}{10}$ or 0·1 metre.

Likewise each decimetre is divided into 10 parts, each called a centimetre (Latin *centi* = 100):

1 centimetre = $\frac{1}{10}$ decimetre = $\frac{1}{100}$ or 0·01 metres,

and finally each centimetre is divided into 10 parts, each called a millimetre (Latin *milli* = 1,000):

1 millimetre = $\frac{1}{10}$ centimetre = $\frac{1}{100}$ decimetre = $\frac{1}{1000}$ or 0·001 metres.

Thus, for example, if an object has a length of two metres, four decimetres, three centimetres, and eight millimetres, we may write them as follows:

2 metres	may be expressed as	2·000	metres.
4 decimetres	,, ,,	·400	,,
3 centimetres	,, ,,	·030	,,
8 millimetres	,, ,,	·008	,,
		2·438	,,

The multiple of the metre, viz. the kilometre or 1,000 metres, is not employed much in scientific laboratory measurement,

though commonly used for measurement of long distances on the Continent. As a unit it corresponds to the British mile, 1 kilometre being about $\frac{5}{8}$ mile (1 metre = approx. 39 inches).

The units of square measure in the metric system are the square metre, square decimetre, etc., the square metre being the area of a square of side one metre. Likewise the units of cubic capacity are the cubic metre, cubic centimetre, etc., i.e. the volume of a cube whose side is one metre or one centimetre. The units of cubic capacity are used not only for measuring the volume of solids but also that of liquids.

The volume of a regular solid can readily be obtained from its linear dimensions, but for a liquid some sort of measuring vessel must be employed. Such measuring vessels are employed extensively in chemical analysis and will be briefly described.

The Measuring Cylinder. This is a narrow cylindrical vessel (Fig. 2) made of glass, and contains, when filled to a definite mark, let us say 100 cubic centimetres of water. Since the diameter of the vessel is constant, if we divide the height of the vessel into one hundred parts, each part will correspond to $\frac{1}{100}$ of the whole, i.e. one cubic centimetre. With such a vessel any number of cubic centimetres of a liquid from one to one hundred can be measured out. Various sizes of these cylinders are usually made, e.g. 100, 250, 500 and 1,000 cubic centimetres.

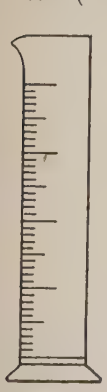


FIG. 2

For liquids, the *litre* is employed as a unit of volume, one litre being equal to 1,000 cubic centimetres (or c.c.). A litre is approximately equal to $1\frac{3}{4}$ pints.

The Burette. This is merely a long tube of uniform bore with a tap at the bottom (Fig. 3). Its capacity is usually 50 c.c. divided into 50 equal parts of 1 c.c. each. Each cubic centimetre is further divided into 10 parts, each of 1 c.c., so that it is possible to *deliver* a quantity of liquid accurately to $\frac{1}{10}$ of a cubic centimetre. The burette is employed extensively in chemical analysis.

Graduated Flasks. These are carefully made flasks gradu-

ated, i.e. marked to *contain* some specified volume of liquid—usually 100 c.c., 250 c.c., 500 c.c., and 1,000 c.c. (Fig. 4).

Pipettes. These are glass tubes with a widened portion in the middle and a graduation mark on the upper stem (Fig. 5). A pipette is filled by suction with the mouth, the liquid allowed to run out till level with the mark and retained in the

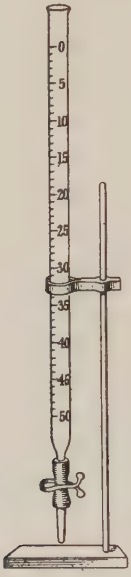


FIG. 3

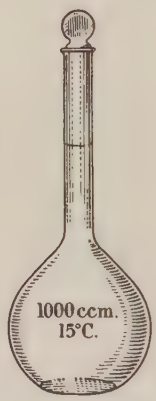


FIG. 4

FIG. 5

pipette by holding the finger firmly on the top. The whole is then transferred to another vessel into which a known volume of liquid (i.e. the capacity of the pipette) is *delivered* by releasing the finger. The usual capacity of a pipette is 5 c.c., 10 c.c., 25 c.c., and 50 c.c., though a pipette to deliver any known small volume can be made.

The unit of weight employed in the metric system is the *gram*. The gram is defined as being the weight of 1 cubic

centimetre of pure water at a temperature of 4° C. (1 pound = approximately 453 grams). The sub-multiples of the gram are :

decigram = $\frac{1}{10}$ or ·1 gram (gm.)
centigram = $\frac{1}{100}$ or ·01 gm.
milligram = $\frac{1}{1000}$ or ·001 gm.

whilst the only common multiple is the kilogram = 1,000 gm. (= $2\frac{1}{5}$ lbs. approx.).

In order to determine the weight of an object we compare its weight with the weight of a standard brass weight. The operation is carried out on a balance, which in principle is a beam pivoted at the centre. If an object hung on one end of the beam exactly balances a standard 10 gm. weight, then that object is said to weigh 10 gm.

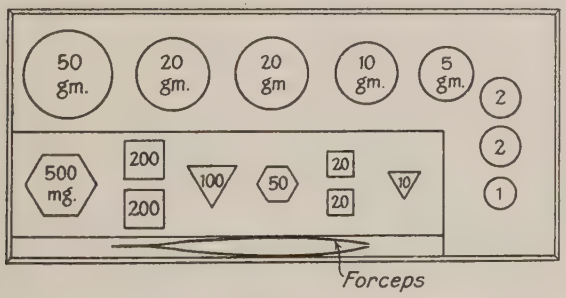


FIG. 6

A common box of weights such as would be employed in an analytical laboratory is usually composed of the following weights arranged in the particular order shown in Fig. 6. The weights larger than a gram are usually round and of brass, whereas the weights less than a gram are flat pieces of metal of the particular shape shown and with one edge turned up to facilitate handling with a pair of forceps. These flat weights are usually marked in milligrams, thus 500 mgm. = $\frac{1}{2}$ gm. or ·5 gm. For example, if in order to balance a given object on a balance, it is found that the following weights need

to be used : 20 gm., 2 gm., 1 gm., 500 mgm., 100 mgm., and two 20 mgm., then the weight of the object would be

	20·000 gm.
	2·000 ,,
	1·000 ,,
500 mgm. =	·500 ,,
100 mgm. =	·100 ,,
20 mgm. =	·020 ,,
20 mgm. =	·020 ,,
	23·640 ,,

DENSITY AND SPECIFIC GRAVITY

The Density of a body is its mass * per unit volume, i.e. it represents the " denseness " or " closeness of packing " of the particles of a body. Thus lead is a heavy substance, while wood is light. This means that in the former case there is packed far more matter per unit of volume than there is in the latter. The measure of the density of a substance is dependent on the units which are employed. In the system employed in scientific measurements where the units are the centimetre, the gram, and the second (the C.G.S. system) for solids and liquids :

$$\text{Density} = \text{no. of gm. per cubic centimetre,}$$

$$\text{or Density} = \frac{\text{mass}}{\text{volume}}.$$

For gases, however, a larger unit of volume is employed, viz. 1,000 c.c. or one litre. On the c.g.s. system, since by definition the weight of 1 c.c. of water at 4° C. is defined as the gram, the density of water at 4° C. is 1 gm. per c.c. or unity. In the

* For purposes of this book, mass may be taken as the same as the weight. Though actually, mass represents the amount of matter in a body and is constant, whilst weight = mass × force due to gravity. This force due to gravity or the earth's pull on a body varies from place to place on the earth. Thus the force due to gravity is not the same on a high mountain as at sea-level ; hence the weight of a body is not the same at high altitudes as at sea-level, yet the mass is the same.

British system where pounds and feet are employed as units, the density of a substance is the number of pounds per cubic foot. Thus on this system the density of water = 62·4 lb. per cu. ft. It will be seen that it is essential that an expression of density should always be accompanied by a statement of the units employed.

The Specific Gravity of a substance is the ratio of its density to that of some standard substance, usually water, at 4° C., i.e.

$$\text{specific gravity} = \frac{\text{mass of unit volume of substance}}{\text{mass of unit volume of water at } 4^\circ \text{ C.}}$$

In the c.g.s. system the lower half of this ratio is unity, so that in this system specific gravity and density are identical numerically. But in the British system, the density of water is 62·4 lb. per cubic feet; its specific gravity is therefore its density divided by 62·4, i.e. unity as in the c.g.s. system, and the specific gravity of any other substance is its density divided by 62·4.

DETERMINATION OF DENSITY

Of a regular solid. This is a comparatively simple matter, since the volume can be readily determined by actual measurement and multiplication. Likewise the weight can be found by the mere operation of weighing and from these two facts the density or mass per unit volume determined.

Of an irregular solid.

(*a*) *A solid unaffected by water.* The volume of such a solid may be found by determining the volume of water which it displaces, e.g. in a measuring cylinder. The weight being known the density can readily be found. This method may be employed, say, to find the density of a glass stopper. It is immersed in water in a measuring cylinder, and the rise in level of the water gives the volume of water displaced and hence the volume of the stopper.

(*b*) *A solid soluble in water or otherwise affected by it.* Either of two procedures may be adopted here. (1) The volume of the substance may be determined by displacement as in (*a*)

above, in some liquid other than water which has no effect on the substance, or (2) the volume may be determined by first coating the substance with a thin coating of varnish or collodion to render it impervious to water and then determining the displacement in water as in (*a*) above.

The density of wheat grains may be found by coating them with collodion in this way to determine their volume. If the weight of the wheat grains be known, their density can be calculated.

Of a Liquid. By the specific gravity bottle. This is a small bottle with a ground-in glass stopper with a hole in it (Fig. 7).

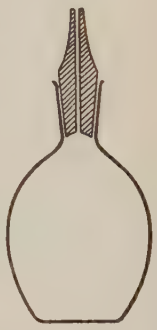


Fig. 7

The method of use is as follows : The empty dry bottle is weighed, filled with the liquid and re-weighed. The liquid is then poured out, the bottle cleaned, filled with water, and weighed again. The volumes of liquid and water employed are the same, so that the ratio of the respective weights of liquid and water gives the specific gravity of the liquid.

In an experiment with chloroform the following results were obtained :

	Weight of empty bottle		10·43 gm.
	,, bottle + chloroform ..		47·74 ,,
∴	,, chloroform		37·31 ,,
	,, bottle + water		35·47 ,,
∴	,, water		25·04 ,,

$$\therefore \text{ specific gravity} = \frac{\text{weight of bottle full of chloroform}}{\text{weight of bottle full of water}}$$

$$= \frac{37{\cdot}31}{25{\cdot}04} = 1{\cdot}49.$$

The specific gravity bottle is used when an accurate result is required and only a relatively small volume of liquid is available for the determination. Where, however, a large bulk of liquid is available and the accuracy required is not great, rapidity of determination being more important, *hydrometers* are employed.

Hydrometers. These are small glass vessels, weighted to varying degrees and arranged to float in the liquid whose density is required. A glass tube about one inch in diameter is weighted at the bottom with mercury or lead shot and tapered to a narrower stem at the top. The weight is so adjusted that the instrument floats with the level of the liquid at the bottom of the narrow stem. If then the instrument is placed in a lighter liquid it will sink lower, e.g. till the level of the liquid is near the top of the narrow stem. The hydrometer is calibrated, i.e. the weight adjusted and a scale indicating the density is fixed inside the narrow stem. Any one instrument can only be used over a short range of density, e.g. ·7 to 1·00, a series of hydrometers being necessary to cover the useful range of density of common liquids. Such a series would contain hydrometers reading ·7—1·00, 1·00—1·30, 1·30—1·600, etc. The hydrometer gives us a useful and rapid method of determining density and is commonly employed for determination of density of:

FIG. 8.—HYDROMETER

(*a*) Sulphuric acid in accumulators.
(*b*) Brine used for refrigerating machines.
(*c*) Mixtures of alcohol and water for excise purposes.
(*d*) Milk.

In the first three cases the density is determined as the quickest method of finding the amount of substance present in the solution, i.e. the concentration of the dissolved substance, whilst in the case of milk the density is often determined with a view to detecting adulteration with water.

APPLICATIONS OF DENSITY

The Chloroform Test for Mineral Matter in Flour. Flour is a mixture of chemical substances. It consists chiefly of starch, with smaller quantities of protein, fat, sugar, cellulose, and mineral matter. The mineral matter or "ash," consisting largely of phosphates, is drawn up from the soil by the wheat plant during its growth, and is normally present in a

flour to the extent of 0·3—0·6 per cent. Any addition of mineral matter, in the form of improvers or self-raising compounds, can be detected by either "ashing" the flour, a somewhat slow process, or by the "chloroform test." The principle on which this test depends is as follows:

The density of chloroform is almost 1·5, whilst that of the mineral matter usually found in flour is *greater* than 1·5; also the density of the remainder of the constituents of flour, viz. starch, etc., is less than 1·5. Thus, if flour be shaken

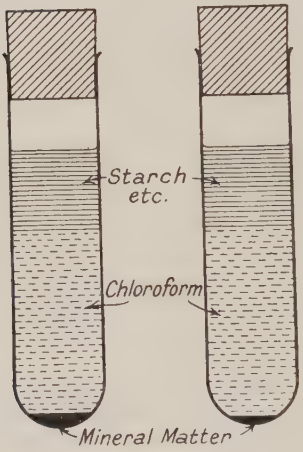


Fig. 9

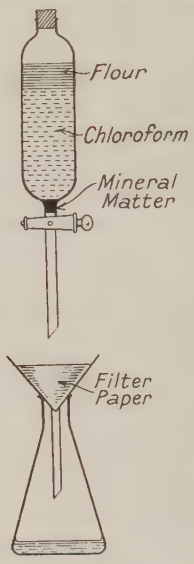


Fig. 10

with chloroform and allowed to stand, the mineral matter will sink to the bottom, whilst the remainder will rise and float at the top. The test may be carried out qualitatively, i.e. by comparing two flours, say, a patent flour and the one under test; the quantity of mineral matter settling out at the bottom may be gauged by the eye (Fig. 9). Thus it is possible to determine whether a given flour has had mineral matter added to it. If it is required to make the test quantitative, i.e. to find out how much mineral matter settles out,

a vessel is used with a tap at the bottom so that the mineral matter can be run off with some chloroform, filtered through a weighed filter paper, dried, and weighed.

The test is usually carried out in a boiling tube or tap funnel about the size of a boiling tube (Fig. 10). The tube is one-third filled with flour (a weighed amount is used if quantitative estimation is to be made), the tube filled almost with chloroform, corked firmly and shaken vigorously for five minutes. On allowing to stand the mineral settles at the bottom and can readily be observed.

Other Applications of Density used in Flour Milling. Differences in density are employed in many commercial operations to separate some undesirable substance present in a mixture. In the milling industry, where much has to be separated before the wheat is fit for milling, it would be surprising if among the various separations effected, those employing differences in density were not to be found. During the course of the dry cleaning of wheat, " air aspiration " is employed extensively. During the early stages of dry cleaning it is necessary to remove husk and light grains from the wheat. This is usually carried out by directing a rapid stream of air through a thin stream of falling wheat. The heavier particles continue to travel onwards in their original direction, falling into a chute prepared for them, whilst the lighter particles are drawn upwards by the stream of air and deposited in the dust collector or in the screening tip. This principle is embodied in Robinson's Wheat Aspirator, a machine often put in before the break rolls to remove light beeswing.

In the case of dust the actual density may be greater than that of the wheat. In fact with many of the particles removed by aspiration there is little difference in their density and that of wheat. It is in the ratio surface area to weight that the difference appears. In the case of the dust this ratio is relatively large compared with that for the wheat. Further, the shape of the particles must be taken into account, as well as density, in separating light grain.

Another instance where difference in density is employed to effect separations is to be found in the wheat washing processes, e.g. in the Turner Concentric Washer (Fig. 11), where the stones are separated from the wheat and the

lighter impurities. A thin stream of wheat is directed evenly around a brass cone. At the base of the cone the wheat meets an uprising stream of water of sufficient force to lift the wheat over the edge of the tank and away to a delivery spout. The

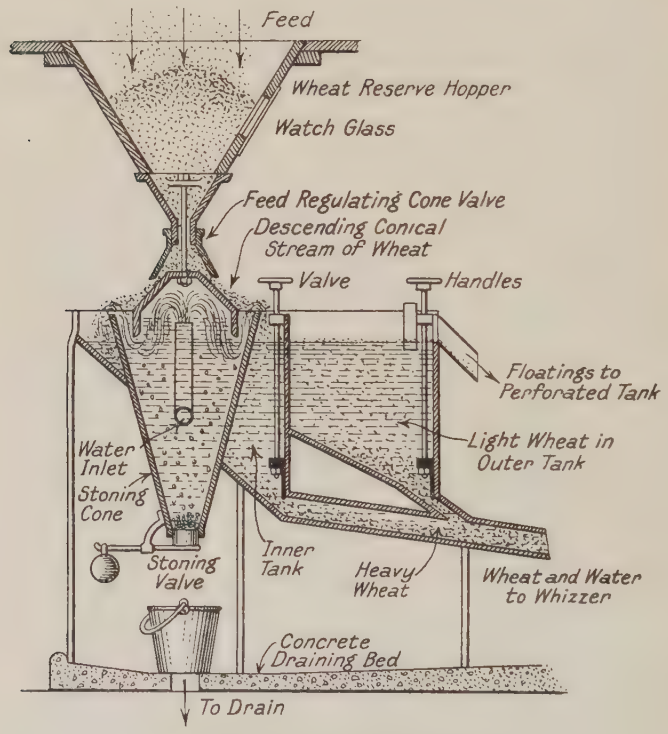


FIG. 11.—TURNER WASHER

stones and sand sink to the bottom of the tank whilst all the light impurities float into a second tank where a few further grains are deposited and the floatings pass to a strainer.

CHAPTER VII

HEAT—THERMOMETRY—SPECIFIC HEAT—LATENT HEAT—HEAT UNITS—MODES OF TRANSFERENCE OF HEAT

Heat has been described as "an imponderable something." It is *not* a kind of matter, since we cannot weigh it or see it. It is only by its effects that we can observe and measure its presence. We detect its presence by its effect on our sense of touch. The word "hot" describes a peculiar condition of a body, corresponding to a certain sensation received by our sense of touch. Cold, as opposed to heat, may be described as absence of heat. We know further that there are degrees of hotness, for we describe one thing as being "hotter" than another. However, our sense of touch is not sufficiently delicate to enable us to distinguish accurately "degrees of hotness" not far removed from each other, and for accurate scientific measurement we must seek some other means.

It is well known that the presence of heat in a substance considerably alters its physical properties. The only property with which we are concerned here is the size of a body. Most substances expand, i.e. get larger, when they are heated, and we shall see that the amount of this expansion enables us to determine the "degree of hotness" or *temperature* of a body.

Expansion of Gases. All gases expand to the same extent when heated to the same temperature. The expansion taking place when 1 c.c. of a gas at 0° C. has its temperature raised by * 1 degree centigrade is about $\frac{1}{273}$ c.c. This expansion is quite appreciable and visible; e.g., if a flask be fitted with a cork and tube as in Fig. 12 and inverted in a trough of water, by placing the warm hand on the flask, the air expands and the level of liquid falls. (Actually it rises slightly first, due to expansion of flask, and then falls.†) The extent to which the level of liquid falls is a measurement of the "degree of hotness" of the hand. Such an instrument

* See page 76.

† Fig. 12 represents the air escaping due to expansion.

is called an *air thermometer*, but owing to the relatively large expansion resulting from a small heat change, it is too delicate to be of very much use for everyday measurement of temperature.

Expansion of Solids. On the other hand we find that solids expand on heating, but by extremely minute amounts.

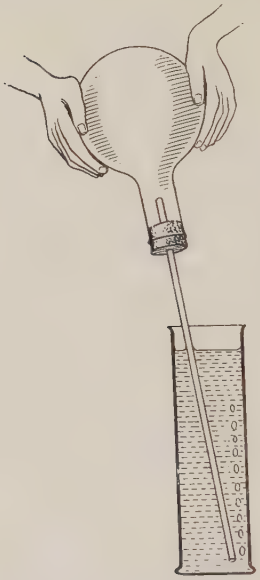


FIG. 12

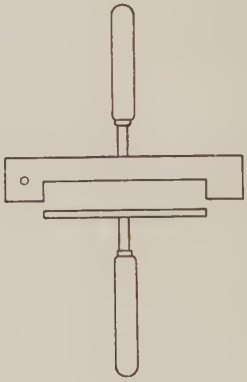


FIG. 13

The fact that solids do expand on heating can be made obvious by an apparatus such as is shown in Fig. 13. When cold, the iron bar fits exactly in the slot and into the hole, but when made red-hot the bar expands by an almost imperceptible amount, yet sufficient to prevent it from fitting into either. The expansion of metals has to be taken into account in the construction of railroad tracks and girder bridges. For railways the rails are usually laid with a short gap between the ends of the lengths in order to allow for

expansion in summer time. Thus it can be seen that the expansion of solids is of no use for the measurement of temperature since it is far too small, whilst in the cases of gases it is inconveniently large.

Expansion of Liquids. Liquids expand to varying extents with rise in temperature, but by quite measurable amounts. If we fill a flask, *a* (Fig. 14) with coloured water, close it with a cork carrying a capillary tube *b*,* and plunge it into hot water, the coloured water expands and the level of the thread of liquid in the capillary tube rises; the narrower the capillary tube the greater will be the rise for any given expansion. The extent of the rise in level of the liquid is a measure of the temperature to which the instrument was subjected. A rise in level of twice the magnitude would indicate roughly a rise of temperature twice as great. Such an instrument is termed a *water thermometer* (thermometer = temperature measurer—*thermos* = heat ; *meter* = measure). A card (Fig. 14, *c*) is often placed behind the capillary tube to enable the rise in liquid to be seen more clearly.

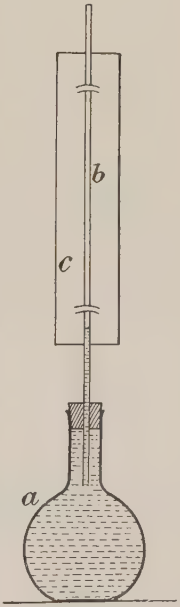


FIG. 14.—WATER THERMOMETER

THERMOMETRY

The water thermometer has only a limited application owing to the fact that at low temperatures the water freezes to ice, and at a moderately high temperature it boils to give steam. The " thermometric " liquid commonly employed is mercury. Mercury is not open to the objection mentioned above in connection with water, also it does not " wet " the glass, and it has quite a reasonable expansion for a small rise in temperature.

Common mercury thermometers consist merely of a capillary tube of uniform bore, at the end of which is blown a

* Capillary tube = one of narrow bore.

bulb. The bulb is filled with mercury and a small portion of the capillary is also filled. The whole is then heated to expel air and sealed at the top while hot so that no air remains in the tube. The thermometer is now ready for "calibrating," i.e. fixing some kind of scale to it to enable us to measure temperature in a certain kind of unit. Firstly two *fixed points* are chosen :

(1) the temperatures at which ice melts,

(2) ,, ,, ,, ,, water boils,

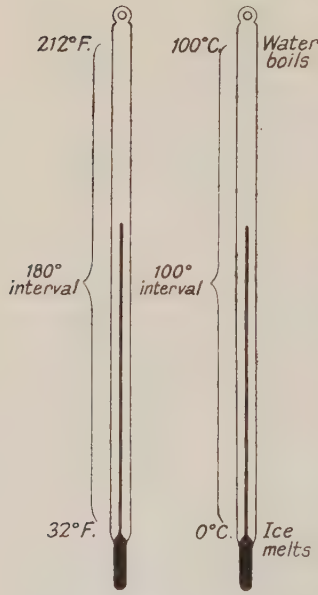


FIG. 15

and these are marked on the instrument, i.e. the thermometer is placed into melting ice, when the mercury contracts and retreats down the capillary tube. The level it finally assumes is marked and termed the *lower fixed point.* The thermometer is then placed in steam, and again the final position of the mercury thread is marked and termed the *upper fixed point.*

It now remains to decide how the thermometer between these two points is to be divided up. In the simplest scale, that known as the *Centigrade scale,* the lowest fixed point is termed 0 and the upper 100, and the intervening space is divided up into one hundred equal divisions, each called *one division Centigrade* or *one degree Centigrade* (abbreviated to 1° C.). The Centigrade scale is employed throughout all scientific measurement, and for commercial purposes on the Continent, though in this country another scale is employed for commercial purposes, viz. the *Fahrenheit scale.*

It will be seen from Fig. 15 that the scales on the two thermometers differ somewhat. Whilst on a Centigrade scale

there are 100 divisions between freezing point and boiling point of water, there are $212 - 32 = 180$ divisions on the Fahrenheit scale, i.e. one division F. or 1° F. indicates a smaller temperature change than 1° C., or

180 divisions Fahrenheit = 100 divisions Centigrade,

i.e. 1 ,, ,, $= \frac{100}{180}$,, ,,

$= \frac{5}{9}$,, ,,

or vice versa 100 divisions C = 180 divisions F.

i.e. 1 division C $= \frac{180}{100} = \frac{9}{5}$ divisions F.

Since the two scales are often used indiscriminately, it is useful to be able to convert a temperature in one scale to that in the other. To do this the main thing to remember is that any given reading in degrees Fahrenheit represents that number of divisions above 0° F., while any reading Centigrade represents a number of divisions above 0° C. which corresponds to 32° F. Therefore before the relation $1° \text{ F.} = \frac{5}{9}° \text{ C.}$ can be applied it is necessary to ascertain the number of divisions above 32° F. our reading is.

To convert 122° F. *to* ° C. :

122° F. represents a point $122 - 32 = 90$ divisions above the freezing point of water.

∴ our required temperature Centigrade will be 90 divisions F. translated into divisions C. above the freezing point of water.

Now $1° \text{ F.} = \frac{5}{9}° \text{ C.}$

$90° \text{ F.} = \frac{5}{9} \times 90 = 50° \text{ C.}$

To convert 50° C. *to* °F.

By inspection it can be seen that 50° C. is half-way between the freezing point and boiling point of water, i.e. 0° and 100°C. Therefore the corresponding point on the Fahrenheit scale will be half-way between 212° and 32°, i.e. $\frac{212 - 32}{2} = \frac{180}{2}$

$= 90°$ divisions,

i.e. 90 divisions above the freezing point, i.e. 32° F.

∴ the actual reading will be $90 + 32 = 122°$ F.

The interconversion of temperatures Centigrade and Fahrenheit can be carried out by the following procedures :

To convert °F. *to* °C.

(*a*) Subtract 32° from the given reading.
(*b*) Translate the result of (*a*) into °C. by multiplying by $\frac{5}{9}$.

To convert °C. *to* °F.

(*a*) Translate divisions C into divisions F by multiplying by $\frac{9}{5}$.
(*b*) Add 32° to the result of (*a*).

EXAMPLE. Convert 98° F. to °C.

(*a*) $98 - 32 = 66$ divisions F.
(*b*) $66 \times \frac{5}{9} = \frac{330}{9} = 36{\cdot}6°$ C.

Convert 15° C. to °F.

(*a*) $15 \times \frac{9}{5} = 27$ divisions F.
(*b*) $27 + 32 = 59°$ F.

NOTE. All temperatures on Centigrade scale corresponding to points below 32° F. are negative.

Thus convert 20° F. to °C.

(*a*) $20 - 32 = -12$ divisions F.
(*b*) $-12 \times \frac{5}{9} = -\frac{60}{9} = -6{\cdot}6°$ Centigrade.

For special purposes, types of thermometer other than the mercury thermometer are employed, e.g. at very low temperatures, temperatures at which mercury freezes to a solid, alcohol thermometers are used. To indicate high temperatures, above or near the boiling point of mercury (678° F. or 359° C.), another instrument is used, termed a *pyrometer*. Pyrometers are often used to indicate the temperature of bakers' ovens or of furnaces, etc. In a common type of pyrometer two strips of different metals are fastened together, and owing to their different rates of expansion the joint strip bends on expansion or contraction, this bend being used to move an indicator over a dial. Another form of pyrometer depends on the fact that a small electric current flows along two connected wires of dissimilar metals, the current depending on the difference in temperature between the two junctions of the wires. One junction is kept at 0° C. or room temperature whilst the other junction is placed at a point at which the

temperature is required to be known. From the current which flows in the wires the difference in temperature of the two junctions can be computed.

Heat Units. A thermometer measures for us the degree of heat or intensity of heat of a body ; it does not measure the quantity of heat in a body. A few particles may each be possessed of a great degree of heat, yet the total quantity of heat possessed by them as a whole may not be so great as the quantity possessed by a greater number of particles at a lower level of heat intensity. The intensity of heat of a red-hot poker is very high, yet the total quantity of heat it possesses will be less than a bath full of hot water, though the intensity of heat of the latter is lower than that of the poker. To measure quantity of heat, we must take account of the quantity of matter present, since each particle contributes its quota to the total quantity of heat, the actual contribution depending on the intensity of heat of the particles.

Since heat is not a material substance and we cannot measure it by weighing it, we measure it by observing its effect on raising the temperature of some standard substance, usually water. Thus we define a *unit of heat* (on the c.g.s. system of units) as the quantity of heat required to raise the temperature of 1 gm. of water by 1° C. (i.e. from 0° to 1° C.). This quantity of heat is termed a *calorie*. The unit of heat on the British system of units is termed the *British Thermal Unit*, and represents the quantity of heat required to raise the temperature of one pound of water through 1° F. This unit is, of course, a much larger one than the calorie (about 250 times as big), but still too small for some purposes, e.g. the sale of coal gas according to its heating value, therefore the gas companies employ for this a much larger unit, the *Therm*, which is 100,000 B.Th.U. (British Thermal Units).

If a gram of water receives heat so that its temperature is raised from 0° to 1° C., it has received 1 calorie ; therefore to raise the temperature of 50 gm. of water from 0° to 1° C. requires 50 calories, and to raise the same quantity of water from 0° to 10° requires $50 \times 10 = 500$ calories ; i.e. the quantity of heat in calories received by any mass of water can be obtained by multiplying its weight in grams by its temperature rise in degrees Centigrade, e.g. a kilogram of

water at the boiling point receives $1{,}000 \times 100 = 100{,}000$ calories. Similarly with the British system, to raise the temperature of:

1 lb. of water from 32°—33° F. requires 1 B.Th.U.
1 lb. „ „ 32°—62° F. „ 30 „
10 lb. (= 1 gallon) of water from freezing point to boiling point, i.e. from 32° F. to 212° F., i.e. 180° F., requires $10 \times 180 = 1{,}800$ B.Th.U.

We can now calculate what quantity of heat (in the form of hot water) must be added to a given amount of cold water in order to raise its temperature to a definite value.

EXAMPLE. How much boiling water must be added to 1 gallon of water at 60° F. in order to raise its temperature to 100° F. (just over blood heat)—1 gallon of water weighs 10 lb.

In order to raise the temperature of 10 lbs. of water from 60°—100° F., i.e. 40° F., it requires $10 \times 40 = 400$ B.Th.U. This quantity of heat is to be supplied by the boiling water.

NOTE. Each pound of water in *cooling* 1° F. *gives out* one B.Th.U., just as one B.Th.U. is *required* to *raise* the temperature of each pound of water.

In giving out its heat the boiling water will fall in temperature from 212° F. to 100° F. (the final temperature) = 112° F. Each pound of water in falling 112° F. gives out 112 B.Th.U.

∴ in order to give out the required 400 B.Th.U. it will be necessary to use $\frac{400}{112} = 3{\cdot}57$ lbs. of water.

∴ In order to raise the temperature of 1 gallon of water from 60° F. to 100° F. requires 3·57 lbs. of boiling water, a little over $\frac{1}{3}$ gallon.

SPECIFIC HEAT

Not all substances have the same heat capacity; i.e. different substances require different amounts of heat in order that their temperatures may be raised to the same temperature; or alternatively equal quantities of two different substances in falling through the same temperature may give out different quantities of heat. Thus if 100 gm. of water at 100° C. be mixed with 100 gm. of water at 0° C., the temperature of the resulting mixture will be 50° C., i.e. the quantity

of heat given out by the hot water in falling through 50° C. is exactly equal to the quantity of heat required to raise the temperature of the cold water by 50° C. But if 100 gm. of lead at 100° C. be mixed with 100 gm. of water at 0° C. the resulting temperature would not be 50° C. but just under 3° C., i.e. the metal in cooling 97° C. has only given out sufficient heat to raise the temperature of the water by 3° C., i.e. it has given it $100 \times 3 = 300$ calories.

∴ 100 gm. of lead in cooling 97° C. give out 300 calories

1 gm. ,, ,, ,, ,, 3 calories

and 1 gm. ,, ,, 1° C. ,, $\frac{3}{97}$ calories

$= \cdot 0309$ calories

Thus 1 gm. of lead in cooling 1° C. gives out far less heat than the same quantity of water falling through the same temperature. Conversely, it requires far less heat to raise the temperature of 1 gm. of lead through 1° C. than it does with water.

The number of units of heat required to raise the temperature of 1 gm. of a substance through 1° C. is termed its *specific heat.** Thus the specific heat of water is 1 and that of lead = ·0309, copper = ·092, flour = ·42.

The specific heat of a body is determined experimentally in either of two ways :

(*a*) The temperature of the body is raised and the heat given out, when it is plunged into cold water found from the rise in temperature of the latter. This method is employed where the body can be heated to a high temperature without damaging it.

(*b*) A known amount of water at a known elevated temperature is added to the body, and the fall in temperature is observed. This method is employed where the body cannot be heated to an elevated temperature.

Method (*a*) is employed in a laboratory determination of the specific heat of a piece of metal, whilst method (*b*) has been employed in the case of flour and malt, etc.

The following values were obtained experimentally in the determination of the specific heat of a brass weight. A brass

* Strictly, Specific Heat = No. of heat units required to raise the temperature of 1 gm. (or 1 lb.) of substance through 1° C (or 1° F) compared with the no. of units required to raise the temperature of 1 gm. (or 1 lb.) of water by the same amount.

weight was heated to 100° C. in boiling water, then rapidly transferred to a known weight of water at a known temperature; the whole was stirred with a thermometer and the highest temperature reached recorded. Such experiments are usually carried out in small copper vessels termed *calorimeters*.

Weight of water	40 gm.
Initial temperature of water	15° C.
Weight of copper calorimeter	50 gm.
Weight of brass	50 gm.
Initial temperature of brass	100° C.
Final temperature	23° C.

N.B.—(A) Actually the initial temperature of the brass was something below 100° C., as its temperature commences to fall as soon as it is removed from the boiling water. (B) In our calculation we must make allowances for the fact that the temperature of the copper calorimeter was also raised from 15° to 23° C. by heat supplied from the brass.

Heat given out (i) = Heat taken in (ii).

(i) The heat was given out by the brass weight in cooling from 100° to 23° C., i.e. 77° C.; now 1 gm. of brass in cooling 1° C. will give out s heat units (where s is the specific heat of brass).

$\therefore$ 50 gm. brass in cooling 77° C. give out $s \times 50 \times 77$ heat units.

(ii) Heat was taken in by two things, viz. the copper calorimeter and the water. Copper has a specific heat = ·1, i.e. 50 gm. copper calorimeter must have received $50 \times \cdot 1 \times 8$ heat units in order that its temperature might be raised 8° (i.e. from 15° to 23°). Also 40 gm. water had its temperature raised 8° C. and therefore received 40×8 heat units.

Now heat given out by brass = heat taken in by calorimeter and water, i.e.:

$$s \times 50 \times 77 = (50 \times \cdot 1 \times 8) + (40 \times 8)$$
$$3850s = 40 + 320$$
$$3850s = 360$$
$$\therefore \quad s = \frac{360}{3850} = \cdot 093$$

i.e. the specific heat of brass = ·093.

This calculation neglects the heat required to heat the thermometer and heat losses taking place while the highest temperature was being reached.

The question of the mixing together of flour and water is of some importance to the baker, since he must know at what temperature to take his mixing water in order to obtain a dough at the correct temperature for fermentation. The following are the results of a laboratory determination of the specific heat of flour.

500 gm. of flour at 20° C. was made into a dough with 500 gm. of water at 40° C., and the temperature of the resulting mass was found to be 34° C. Neglecting the heat required to raise the temperature of the mixing vessel we obtain :

$$\text{Heat given out} = \text{heat taken in.}$$

$$500 \times (\text{fall in temp.}) = 500 \times \text{specific heat} \times \text{rise in temp.}$$

$$500 \times 6 = 500 \times s \times 14$$

$$3000 = 7000\, s$$

$$\frac{3000}{7000} = s$$

i.e. $$s = \frac{3}{7} \text{ or } \cdot 43 \text{ (approx.)}$$

i.e., in order to raise the temperature of a gram of flour 1° C. (neglecting yeast and salt), it requires ·43 calories. (Minor adjustments reduce this to 0·42 ; see p. 81.)

Example to illustrate how the specific heat of flour may be used. At what temperature should water (140 lbs.) be taken, in order that, when mixed with flour (280 lbs.) at a temperature of 60° F., a dough at 80° F. will be produced ?

Neglecting any heat losses due to the vessel, etc. :

$$\text{Heat given to flour} = 280 \times \text{rise in temp.} \times \text{specific heat of flour.}$$

$$= 280 \times 20 \times \cdot 42$$

$$= 2352 \text{ B.Th.U.}$$

This amount of heat must have been derived from 140 lbs. of water falling from t° to 80° F.

i.e. heat given out by water = 140 × (fall in temperature) =

$$140 \times (t - 80°)$$

$\therefore$ since these heat quantities must balance,

$$140 \times (t - 80) = 280 \times 20 \times \cdot 42$$

i.e. $$140t - 11200 = 2352$$

$\therefore$ $$140t = 2352 + 11200 = 13552$$

$\therefore$ $$t = \frac{13552}{140} = 96{\cdot}8^\circ \text{ F.}$$

i.e. the required temperature is 96·8° F.

CHANGE OF STATE—MELTING POINT AND BOILING POINT—LATENT HEAT

We have already seen that when a solid is heated it commences to expand and its temperature rises. If the heating be continued so that the temperature goes on rising, there will be reached ultimately a point at which the solid commences to melt and change to a liquid. The temperature at which this occurs is quite definite and fixed for any pure substance and is termed the *melting point*. If the heating be continued, the temperature of the liquid formed will rise until another point is reached, when a further change in state occurs, i.e. the liquid vaporises or boils. The temperature at which this occurs is termed the *boiling point*, and like the melting point is quite definite and is one of the physical " constants " of the substance. Any further heating of the vapour results in further expansion and rise in temperature but no change in state ; e.g. superheated steam is an example of such a highly heated vapour.

When heat is being supplied to a solid, the temperature gradually rises until the melting point is reached. Then, even though heat is still being supplied, the temperature does not rise further until the whole of the solid has been converted to liquid, then the temperature commences to rise again. In other words the temperature remains constant at the melting point as long as the substance is melting. What becomes of the heat that is being supplied during the melting process ? It is not made evident by a rise in temperature, and is therefore probably used up in some way in melting the solid.

That heat is required in order to melt a solid *without*

raising its temperature can readily be shown, e.g. in the case of ice. If some ice be stirred in a beaker, the temperature indicated on a Centigrade thermometer will be 0° C. If the stirring be continued and a small gas flame be placed under the beaker, the ice will commence to melt, but the temperature will not rise above 0° C. until the whole of the ice has melted. The heat from the gas flame is then being used up in melting the ice. Further, if we take two beakers and into one, place 10 gm. of ice and into the other 10 gm. of ice-cold water (i.e. water at 0° C.), they will both have the same temperature. If now we add to each of these two vessels the same amount of heat, say to each 800 calories in the form of 20 gm. of water, at 40° C., we shall find that in the case of the ice the final temperature attained will still be 0° C., whilst the temperature of the ice-cold water will become raised to about 27° C.

In the first case the whole of the heat supplied is used up in changing the solid ice to water, whilst in the second case the whole of the heat is available for raising the temperature of the cold water. This heat which is required to convert a solid to a liquid is termed *latent heat* (latent = hidden), and it remains hidden in the liquid until the liquid is converted back again to a solid, when it is liberated. This behaviour is quite general when a solid is converted to a liquid ; and we define *latent heat* as the number of units of heat required to convert 1 gm. of a solid to a liquid *without raising its temperature*. In the case of ice the latent heat is about 80 calories, i.e. it requires 80 calories to convert 1 gm. of ice to 1 gm. of water at 0° C. Precisely similar changes take place when liquids are converted to vapours, i.e. it requires heat to convert a liquid to a vapour without raising its temperature. In the case of water to steam, it requires about 536 calories to convert 1 gm. of water at 100° C. to 1 gm. of steam at 100° C. This is termed the *latent heat of vaporisation* of steam, and the heat remains hidden in the steam until it condenses again to water. Thus a gram of steam on condensing to water liberates enough heat to raise the temperature of 536 gm. of water (nearly a pint) by 1° C. or liberates as much heat as is present in 5·36 gm. (about a teaspoonful) of boiling water (100° C.).

MODES OF TRANSFERENCE OF HEAT

There are three modes of transference of heat; i.e., heat may be transferred from one body to another in either or all of three ways. These are termed (*a*) Conduction, (*b*) Convection, (*c*) Radiation.

Conduction. If one end of an iron poker be placed in the fire, after a very short space of time the end furthest from the fire becomes sensibly hot, i.e. heat has passed from one end of the poker to the other. In order to account for this transfer of heat along the poker, it is supposed that the latter is composed of a large number of minute particles, each of which gets warm and passes the heat on to its neighbour till eventually it reaches the end of the poker. Thus the characteristic feature of this mode of heat change is that it requires some material substance to pass the heat along, although the heated particles themselves do not actually move. A substance like iron, or metals generally, which conduct heat readily are termed *good conductors* of heat, whilst those substances like wood, glass, air, water, which do not conduct heat at all readily are termed *poor* or *non-conductors* of heat.

The actual conductivity of a material is determined by finding how much heat passes through unit surface area of a block of unit thickness in unit time.

Apparatus in which heat is required to pass quickly is usually constructed of metals, e.g. a boiler or kettle; here, heat from the fire or gas is conducted as rapidly and completely as possible to the water inside. Apparatus in which it is required to conserve heat, i.e. the heat losses must be as little as possible, is constructed of non-conducting materials, or alternatively covered or " lagged " with a layer of non-conducting material. Thus pipes conveying steam are usually " lagged " with asbestos packing to bring the heat losses to a minimum.

The common " Thermos " or " Dewar " flask is a two-walled vessel with a vacuum in the space between the two walls. This " vacuum " is the best of all non-conductors, for there is no matter present at all there, and consequently heat is only transferred from the inner vessel to the outside air at

a very slow rate. Cold liquids remain cold and hot liquids retain their heat for a longer period than they would if kept in an ordinary vessel.

Convection is the process whereby fluids (i.e. gases or liquids) become heated by actual movement of their particles, due to differences in density of the individual heated particles, Consider a large tank of cold water (Fig. 17) heated by a

FIG. 16.—DEWAR FLASK

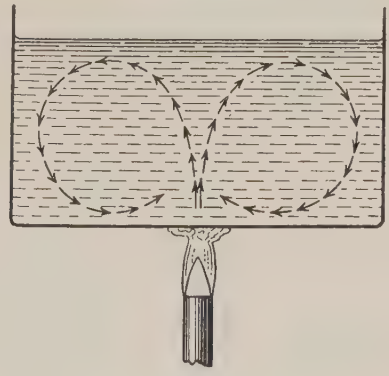


FIG. 17

small gas flame at a point at the bottom. The particles of water immediately above the gas flame become heated by conduction through the walls of the tank. Now, water on being heated expands, i.e. the density of the warm water particles would be less than that of the cold water particles.

Density $= \frac{\text{mass}}{\text{volume}}$; and since the mass remains the same and the volume increases, the density must diminish. The light, warm particles tend to rise to the surface, their place being taken by cold particles, which in turn become heated and rise. A " drift " or current is set up in the liquid until eventually the whole of the particles in the tank become heated. Such currents are termed *convection currents*, and the water becomes heated by convection.

This principle of heating by convection currents is made use of in the common household hot water supply. The hot

water from the boiler rises, and its place is taken by cooler water.

Convection currents are even more marked in gases, where greater expansions occur with small rises in temperature. The ventilation of an ordinary room is accomplished by means of convection currents. An ordinary fire depends for its successful working on convection currents. The air in the chimney gets heated and rises, whilst fresh air is drawn into the room over the fire into the chimney, where it eventually suffers a similar fate.

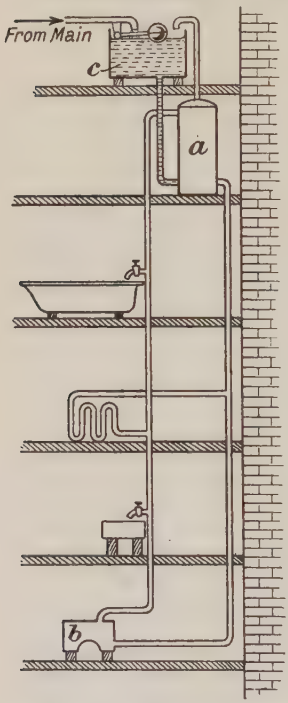


FIG. 18.—HOT WATER SYSTEM OF A HOUSE

a, hot water tank.
b, boiler. *c*, Feed tank.

Radiation. This mode of transference of heat is essentially different from the two previous modes in that it requires no material substance for transmission and that radiated heat travels in straight lines in the same manner as does light; e.g. the hand held in front of a fire receives heat by radiation from the fire, the intervening air plays no part in the transmission and does not even have its temperature raised. Bread is baked in an oven by the heat radiated from the oven walls. The so-called "Water Radiator" depends for its use partly on convection currents and partly on radiation.

The essential feature of radiation is that the matter receiving the heat is not in direct contact with the matter sending it out and the intervening space is not affected. We receive heat from the sun solely by radiation.

So-called radiators are employed in some types of wheat conditioners, e.g. Robinson's "Mallinson." Hot water radiators or rows of steam pipes are arranged in the upper or heating section of the conditioner. The wheat passes down

over the radiators and is heated by actual contact, i.e. the wheat becomes heated by conduction, not radiation. At the same time hot air currents are drawn through the wheat stream. Thus the mass of wheat gets hot partly by air currents and partly by conduction of heat from grain to grain. The disadvantage of this type of conditioner is that the moisture content of the grain coming from the machine varies. This is due doubtless to the fact that the grains coming in direct contact with the radiator get heated to a higher temperature than those which do not. Wheat is a poor conductor of heat, therefore the outer grains, in so far as they are heated by conduction, are not so warm as the grains touching the " radiator." In view of this, the descending column or stream of wheat is turned over at stages in its descent.

CHAPTER VIII

PRESSURE IN GASES—ATMOSPHERIC PRESSURE—PUMPS

Pressure in Gases. Matter can exist in either of three states: as a solid, a liquid, or a gas. The two last are often grouped together as " fluids " since they flow. Thus a solid retains, indefinitely, its own shape unless force be applied to change it, whilst fluids flow from one shape to another under their own weight and acquire the shape of the vessel into which they are placed, quickly if " mobile," and slowly if " viscous." Further, liquids and gases differ in one important feature. Though liquids will adapt themselves to the shape of the vessel in which they are placed, no change in pressure will alter their volume (or at most only to a slight extent). That is, they are practically incompressible; a gallon of water cannot be forced to occupy any other volume than a gallon either by increasing or diminishing the pressure on it. A gas, on the other hand, always tends to occupy as large a volume as possible if left to itself, or it may readily be compressed into a small volume, though there is always a limit to this process. Almost any amount of air may be compressed into a closed box, or part of the air may be removed by means

of a pump. But whatever air remains in the box occupies the whole of the space. Thus the volume occupied by a gas is intimately connected with the pressure to which it is subjected. The relation between the volume and the pressure of a gas at any given temperature was discovered by Robert Boyle (1662), and is known in England as *Boyle's Law*. It states that the volume of a gas is inversely proportional to the pressure, provided the temperature remain constant, i.e. the greater the pressure the smaller the volume. Thus if P be the pressure of a gas of volume V,

then at pressure $2P$ the volume will be $\frac{V}{2}$,

and at $\frac{P}{2}$,, ,, $2V$,

or at $3P$,, ,, $\frac{V}{3}$,

From which it will be seen that the product of the pressure and the volume is a constant, namely PV, since

$$2P \times \frac{V}{2} = \frac{P}{2} \times 2V = 3P \times \frac{V}{3} = PV.$$

Boyle's Law may thus be stated: at constant temperature the product of the pressure and the volume of a gas is constant

This law is not absolutely exact, though it is surprisingly accurate for pressures below about 10 atmospheres (150 lbs. per sq. in.):

Gases being material substances have weight, although their density is usually very small compared with that of solids or liquids. For a reference standard for density, water would be inconveniently large. Thus 1 c.c. of water at 100° C. gives 1,603 c.c. steam, and since the density of water at 100° C. is 0·9584 (i.e. 1c.c. weighs 0·9584 gm.), then 0·9584 gm. of water at 100° gives 1,603 c.c. steam.

$\therefore$ 1 gm. water at 100° would give $\frac{1603}{0{\cdot}9584}$ c.c. steam $= 1672$ c.c.

$$\therefore \quad \text{Density of steam at } 100° = \frac{1}{1672} = {\cdot}000598$$

Thus, compared with water, steam has a density of only ·000598.

Hydrogen, the lightest gas known, is usually taken as the standard for gases, 1 c.c. of hydrogen at 0° C. and 760 mm. weighs about ·00009 gm.

Early philosophers disputed the material nature of air, and it was not until air was actually weighed that it was recognised that it is like other kinds of matter in this respect. The weight of air can be determined by withdrawing all the air from a glass globe and then weighing it. On admitting air and reweighing it is found that 1,000 c.c. (a litre) of air at 0° C. and 760 mm. weigh about 1·3 gm. For expressing densities of gases the temperature and pressure under which the determination is made must be stated, since gases so readily undergo changes in volume, and hence in density, with changes of temperature and pressure.

Since air, then, has weight, it must exert a pressure on all surfaces exposed to it, and it is further obvious that this pressure will be the less the more we ascend into the atmosphere.

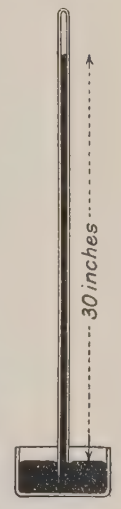


FIG. 19

The Barometer. The actual measurement of the pressure due to the atmosphere was first made by Torricelli (1643), who devised the mercury barometer. In its simplest form this consists of a glass tube about 33 inches long and closed at one end (Fig. 19). The tube is completely filled with mercury, the open end closed with the finger, and the instrument inverted in a trough of mercury. On removing the finger it is found that the level of the mercury sinks, leaving a space at the top of the tube. The height of the column of mercury above the surface in the trough will be found to be about 760 mm. or 30 ins., i.e. the pressure on the surface of mercury in the trough due to the weight of the super-incumbent column of air on it is able to hold up a column of mercury 30 ins. high. Thus the height of the barometer measures the pressure of the atmosphere. The atmospheric pressure varies from time to time but never far from 760 mm. or 30 ins., and these variations are employed to predict weather changes by reason of certain relations between the two.

Since mercury has a density of 13·6, i.e. it is 13·6 times as

heavy as water, the atmosphere will hold up a column of water 13·6 times as high as with mercury, i.e. 30 × 13·6 ins., or 2·5 × 13·6 = 34 feet; i.e. we might use a barometer tube filled with water to measure atmospheric pressure, but it would need to be inconveniently long, viz. over 34 feet.

A water barometer would, of course, be much more sensitive than a mercury one, namely 13·6 times as sensitive, but difficulty in maintaining the vacuum at the top is encountered

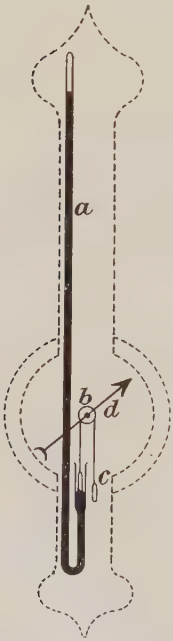


FIG. 20.—WEATHER GLASS
a, Barometer tube. *b*, Pulley.
c, Weights. *d*, Pointer.

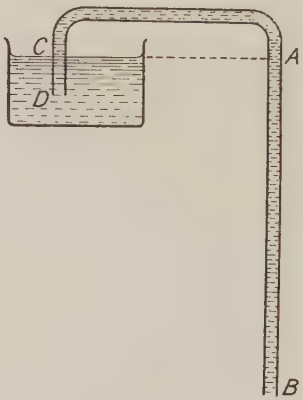


FIG. 21.—SYPHON

when water is used because of the tendency of water to vaporise at ordinary temperatures.

Barometers on which the atmospheric pressure is read from a dial, consist of a U tube with limbs of unequal length

(Fig. 20). When the mercury rises in one limb, it falls by a corresponding amount in the other limb. The height of the barometer is the difference in level of the mercury in the two limbs and is read off on a graduated dial.

The Syphon is a tube bent twice at right angles, with one limb longer than the other. It may be employed for withdrawing a liquid from a vessel which has no outlet at the bottom. If we imagine such a syphon as BACD, suppose the ends be closed temporarily. On opening end D no liquid will flow downwards from DC since the height DC is less than the barometric height. The pressure at A must be equal to that at C, since both are at the same level; this pressure is equal to the atmospheric pressure. Therefore the pressure inside the tube at B is greater than atmospheric pressure by an amount equal to column of liquid AB, and if the tube be opened at B liquid will tend to run out. The atmospheric pressure on the surface of the liquid at C will keep DC full of liquid, so that as liquid runs out at BA fresh liquid fills into DC producing a continuous stream.

The essentials of the syphon are:

(1) That the outlet is below the level of liquid in the vessel being emptied. (2) The total height of the syphon above the level of the liquid in the vessel must be less than the barometric height for that liquid.

Simple Water Pumps. (1) Those depending on the principle that atmospheric pressure is capable of supporting a column of water whose height does not exceed the height of the water barometer, viz. about 34 feet.

The Common Suction Pump (Fig. 22). A long pipe B connects the pump proper with the source of water. The head of the pipe B is fitted with a valve A operating upwards. The barrel of the pump carries a piston actuated by a rod. The piston also carries a valve D, which operates upward. When the pump is in use the upward stroke of the piston and rod opens valve A and closes D. Thus the pressure below the piston is reduced and water is forced up the pipe by the atmospheric pressure acting on the surface of the water in the well. It will be obvious that the height to which the water can be raised cannot exceed the height of a water barometer. If the height is greater than that of the water

barometer, then a vacuum or partial vacuum will form in pipe B and the water will rise no farther.

On the downward stroke of the piston, valve A closes and D opens, the water between the valves being forced above the piston D. On the next upward stroke this water is raised to the spout C where it overflows and more water enters the barrel of the pump via the valve A. Thus the use of the common suction pump is limited to raising water from depths not greater than the height of the water barometer, viz. about 34 feet. In practice 30 feet is the limit.

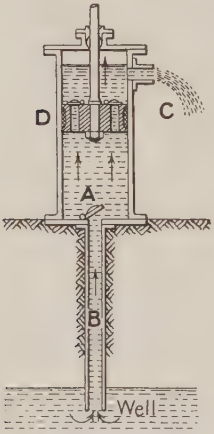


FIG. 22.—SUCTION PUMP

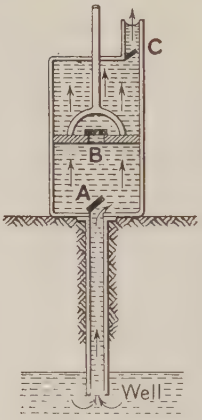


FIG. 23.—LIFT PUMP

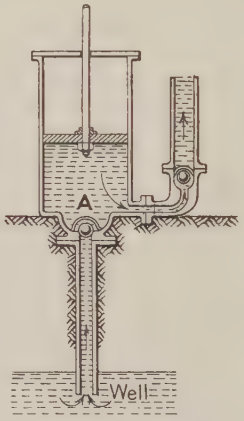


FIG. 24.—FORCE PUMP

If it is required to raise water from a depth greater than 30 feet, then the pump must either be installed at a height of 30 feet above the surface of the water or some other device must be adopted.

The Lift Pump (Fig. 23) may be employed to raise water from a height not exceeding the height of the water barometer, and to pump it to almost any desired height above the barrel. The lift pump is a modification of the common suction pump with an additional pipe and valve to carry the water to the desired height.

Another modification which will lift water the height of the water barometer and pump it to any desired height is the

Force Pump (Fig. 24). In this pump there is no valve in the piston but instead a valve in the pipe conducting the water upwards. Force pumps are usually employed in fire engines. The piston is actuated by steam power and has a double action (Fig. 25). The piston P, moving in the direction indicated by the arrow, opens valve F and draws in water, at the same time forcing out water through the other valve F. On the return stroke, valves V open and allow water to

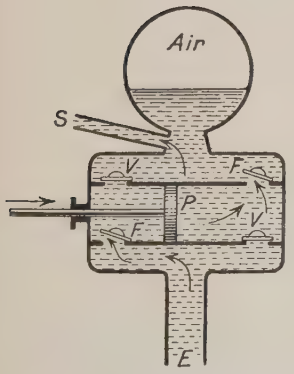


FIG. 25
Double acting force pump.

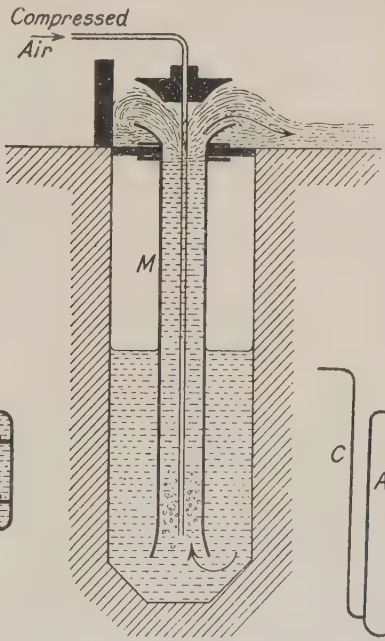


FIG. 26.—AIR LIFT

FIG. 26*a*

enter and escape. The air vessel acts as a kind of reservoir. The air in it becomes compressed and thereby maintains a continuous flow of water, thus overcoming the momentary stoppage when the piston reverses.

(2) The commonest method of raising water from a well whose depth exceeds the height of the water barometer is by means of an *Air Lift* (Fig. 26). The principle of the air lift is

as follows: compressed air is delivered to the bottom of a "rising main." The rising main A (Fig. 26*a*) is made the longer limb of a U tube, the shorter limb B containing the water to be pumped. The longer limb becomes filled with water aerated with air, the whole having a lower density than the unaerated water in the shorter limb. Thus the longer column of lighter aerated water is balanced by the shorter column of heavier unaerated water. In practice the pipe corresponding to the lower limb is omitted. The water in the well acts as the lower limb.

The actual material in the rising main may be either short columns of liquid separated by bubbles or cylinders of air, or a homogeneous mixture of water and very small bubbles of air. The depth from which the water may be raised depends on the proportion of air to water in the aerated column, i.e. on the density of the aerated column as compared with the unaerated column. In general the depth of immersion of the main is about $1\frac{1}{2}$ to 2 times the lift, though the theoretical *optimum* conditions must be worked out for each case.

Simple Air Pumps. These may be divided into two main groups:

(*a*) Those for compressing air.
(*b*) Those for exhausting the air from a vessel.

More strictly class (*a*) are termed condensing pumps or "compressors."

In the main their principle is the same as that underlying the use of water pumps.

(*a*) *Condensing Pump or Compressor.* In principle this consists of a chamber or barrel carrying a piston P (Fig. 27). The piston carries a valve V, which opens towards the vessel in which the air is being compressed. Near the end of the barrel communicating with the air vessel (called the receiver, A) is a second valve, F, which operates in the same direction as valve V. In the forward stroke the air between V and F becomes compressed, forces open valve F and passes into the receiver. Thus the air in the receiver is now at a pressure greater than that of the atmosphere. When the return stroke is commenced the excess pressure in the receiver closes

valve F, and as the piston is withdrawn the atmospheric pressure opens valve V. When the forward stroke is commenced again both valves remain closed until the air in the barrel is compressed to a pressure equal to the pressure of the air in the receiver, when valve F opens to admit the compressed air to the receiver. Theoretically, all the air which enters the barrel is forced into the receiver at the forward stroke, and there is no limit to the pressure which can be attained in the receiver. Actually, due to leakages around the piston and to the fact that a " clearance " space is left between valve F and the nearest position of the piston, such ideal conditions are not obtained.

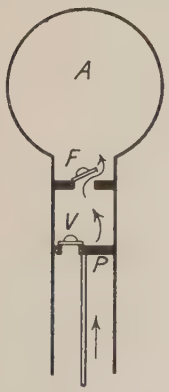


FIG. 27.—COMPRESSOR

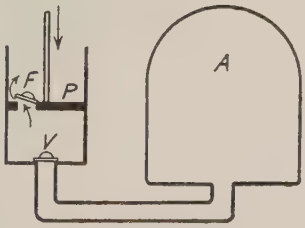


FIG. 28.—EXHAUST PUMP

(*b*) *Air Pump for exhausting air from a vessel.* This is similar in construction to the compressor, the main difference being the operation of the two valves. These operate away from the receiver or vessel being exhausted. On the first withdrawal stroke of the piston, valve V (Fig. 28) opens and valve F closes ; air is thus drawn from the receiver. On the first part of the downward stroke, V closes and F remains closed until the air between the valves is compressed to atmospheric pressure, when F opens. During the remainder of the downward stroke F remains open and allows air to escape from beneath the piston. At each stroke less and less air is removed from the receiver, and the pressure in the receiver falls until

it is no longer sufficient to raise the valve V ; consequently a perfect vacuum is never attained with such a pump. The valves are constructed of much lighter material than for water pumps ; sometimes thin sheet rubber is used or oiled-silk covering a number of fine holes in the piston.

Pumps for attaining very low vacuum are mechanically operated. In addition the valves themselves are mechanically operated, thus obviating the difficulty of moving the valves at low vacua.

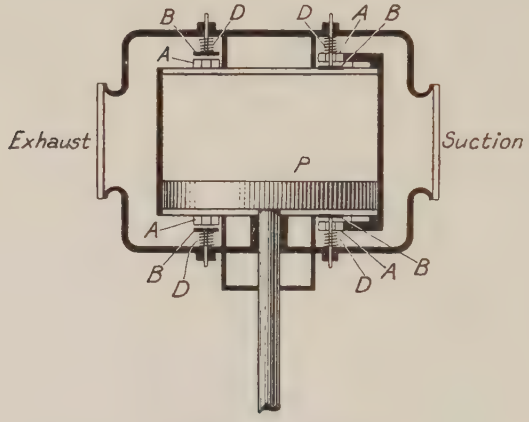


FIG. 29.—AIR PUMP
AB, valve. *D*, valve spring. *P*, piston

Vacuum Pumps used in Flour Mills. Mechanically operated vacuum pumps are employed in flour mills as part of the plant for a pneumatic or suction intake. The parts of the plant of immediate interest are the air pump and the receiving chamber for separating the air from the grain with some form of " air lock " for discharging the grain without losing vacuum.

The Air Pump. This is a vertical medium-speed short-stroke pump actuated either by steam or an electric motor. Owing to the amount of dust passing through the pump, either dry lubrication or no lubrication at all is used. The valves consist of small circular steel plates held in position by light springs (Fig. 29).

On the upward stroke the upper right-hand and lower left-

hand valves close, air is drawn in below the piston at the lower right-hand valve and air above the piston is forced out at the upper left-hand valve. On the downward stroke these conditions are reversed, air is drawn in at the top right-hand valve and air below the piston ejected at the lower left-hand valve. Connected to the pump are the receiving

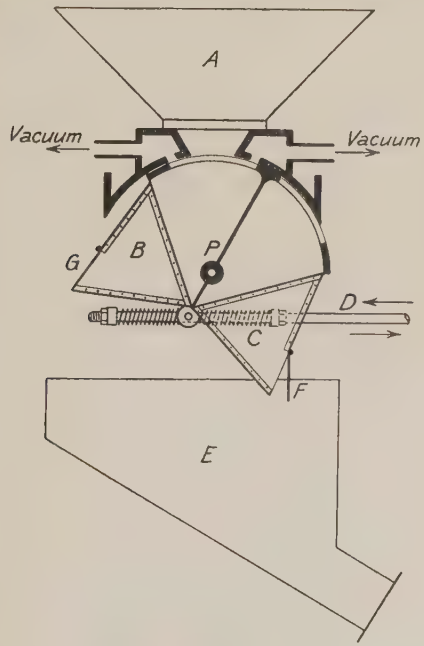


FIG. 30.—TIPPING BOX

A, wheat feed. *B,C*, boxes. *D*, control rod.
E, delivery hopper. *F,G*, doors. *P*, pivot.

chamber and pipe lines. After the grain has passed along the pipes it reaches a receiving chamber. The air and grain enter the receiving chamber with a considerable velocity, but owing to the large size of the chamber compared with the grain pipes the velocity is reduced and the grain separates by gravity from the air. The grain settles in the lower part of the vessel while the air is drawn off from the upper part.

Beneath the receiving chamber is a device for allowing the grain to escape without allowing air to enter. This " airlock " consists of either of two devices : (*a*) the Tipping Box, (*b*) the Rotary Discharger.

(*a*) *The Tipping Box* (Fig. 30). This consists of two pivoted boxes, side by side. The weight of the grain discharging into

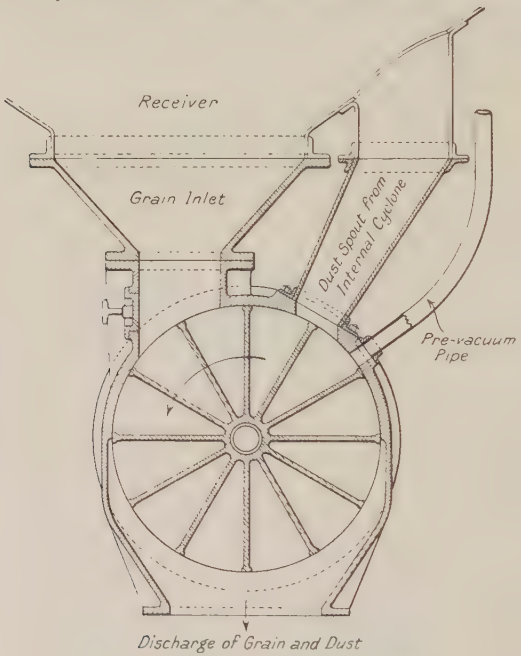


FIG. 31.—ROTARY DISCHARGER

one box causes it to tip over and bring the entrance to the second box opposite the outlet from the main receiving chamber. The full box then discharges its contents from the bottom through an automatic door which opens immediately the vacuum is cut off by the box tipping over. In some improved patterns of this device the box is tipped over mechanically.

(*b*) *The Rotary Discharger* (Fig. 31) consists of a wheel with

a series of compartments which receive the grain from the bottom of the receiving chamber. The wheel revolves slowly and delivers the grain into a hopper.

CHAPTER IX

VAPOUR PRESSURE AND HYGROMETRY

Partial Pressure. Perhaps the most characteristic property of a gas is its power of filling completely the vessel into which it is placed. Let us now apply this knowledge to a study of mixtures of gases. To simplify matters we will first of all stipulate a constant temperature. Consider a vessel capable of holding five litres of oxygen at atmospheric pressure. It will, of course, be full of oxygen at this pressure. If we put only one-fifth of the amount of oxygen in the vessel, it will still be full of oxygen, but the pressure will now be only one-fifth of atmospheric pressure (Boyle's Law). The vessel will obviously accommodate, instead of oxygen, five litres of nitrogen at atmospheric pressure, or if only four-fifths of this quantity of nitrogen be admitted, the vessel will be full of nitrogen at a pressure of four-fifths of an atmosphere. If now, instead of pure oxygen or nitrogen, we introduce into the vessel one litre of oxygen at one atmosphere pressure and four litres of nitrogen at one atmosphere pressure, we shall obtain a vessel *full* of oxygen at one-fifth atmosphere pressure and *full* of nitrogen at four-fifths atmosphere pressure, and the total pressure within the vessel will be $\frac{1}{5} + \frac{4}{5} = 1$ atmosphere, i.e. the vessel will contain five litres of mixed gas at one atmosphere pressure. This is really only another way of saying that, if the gases were separated, we should have one litre of oxygen at one atmosphere and four litres of nitrogen at one atmosphere, but the former is evidently a much more accurate description of the true state of affairs. We may generalise the foregoing statements in the form of Dalton's Law of Partial Pressures, which states that : " in any mixture of gases, each exerts its own pressure independently of the others, and the total pressure of the mixture is the sum of the partial pressures of the components."

Thus, if we take a five-litre vessel and force into it

1	litre of	oxygen	measured at	1	atmosphere	pressure.
2	,,	nitrogen	,,	,,	,,	,,
3	,,	hydrogen	,,	,,	,,	,,
4	,,	carbon monoxide	,,	,,	,,	,,
5	,,	nitrous oxide	,,	,,	,,	,,

the vessel will contain

5	litres of	oxygen	at	$\frac{1}{5}$	atmospheres	pressure.
5	,,	nitrogen	,,	$\frac{2}{5}$	,,	,,
5	,,	hydrogen	,,	$\frac{3}{5}$	,,	,,
5	,,	carbon monoxide	,,	$\frac{4}{5}$	,,	,,
5	,,	nitrous oxide	,,	1	,,	,,

The total volume will be five litres and the total pressure three atmospheres.

The same result can be arrived at in another way by noting that the amount of gas at one atmosphere to be forced into the 5-litre vessel is $1 + 2 + 3 + 4 + 5 = 15$ litres and that therefore the final pressure will be 3 atmospheres (Boyle's Law).

Vapour Pressure. Although a liquid changes completely into a vapour at its boiling point, it is a matter of common observation that a liquid, left in the open at a temperature below its boiling point, will evaporate, and that, in general, the higher the temperature the more rapidly does the evaporation proceed. This tendency to evaporate may be measured by a property characteristic of the liquid known as the "vapour pressure." Consider a liquid in an evacuated vessel at a constant temperature. The liquid will tend to evaporate, but at the same time vapour so formed will tend to condense, and it is found that for any liquid evaporation occurs under these conditions until the vapour so formed exerts a certain definite pressure which depends only on the nature of the liquid and the temperature. If the pressure of the vapour is below this vapour pressure, then more liquid will evaporate until this definite vapour pressure is attained. If, on the other hand, the pressure of the vapour is larger than this value, vapour will condense until the same definite vapour pressure is reached. The vapour pressure increases with the emperature very rapidly. These considerations apply to

cases where the liquid and vapour only are present in the vessel, but from Dalton's Law of Partial Pressures it will be seen that the presence of some other gas or vapour will not affect the conclusions since each gaseous constituent of the mixture exerts its own pressure independently of the others. The only liquid whose vapour pressure concerns flour milling students is water and the variation of vapour pressure with temperature is given in the following table :

Temperature $t°$ *C.*	*Vapour Pressure in mms. mercury*
0	4·58
2	5·29
4	6·10
6	7·01
8	8·04
10	9·21
12	10·52
14	11·99
16	13·63
18	15·48
20	17·54
22	19·83
24	22·38
26	25·21
28	28·35
30	31·84

Thus, if air at 760 mm. pressure is placed in contact with water at 16° C., the final pressure of the mixture will be $760 + 13{\cdot}63 = 773{\cdot}63$ mm., and the barometer would read this value, since the barometer always indicates the total pressure and not the pressure due to oxygen and nitrogen (i.e. air) alone.

Hygrometry. Measurements and calculations dealing with the quantity and pressure of water vapour in the air are dealt with under the term *hygrometry*, and instruments employed for these measurements are termed *hygrometers*. The amount of water vapour in the air is not constant. The maximum quantity which can be present is fixed by the vapour pressure and therefore depends only on the temperature. But it frequently happens that there is not sufficient water available to give enough vapour to reach this pressure. The air, or strictly speaking, the *space* occupied by the air, is then said

to be *unsaturated*. The dampness, or as it is called *humidity* of the air, therefore depends on the temperature and the climatic conditions, the former fixing the upper limit. The following table shows the relative proportions of water vapour and air in 1 cubic metre of saturated air, when the barometer stands at 760 mm.

t° C.	*Pressure due to water vapour in mm.*	*Pressure due to air in mm.*	*Wt. of dry air in 1 cu. metre of saturated air in gm.*	*Wt. of water in 1 cu. metre of saturated air in gm.*	*Wt. of water vapour per kgm. of dry air in gm.*
10	9·21	750·79	1236	9·39	7·59
12	10·52	749·48	1227	10·63	8·67
14	11·99	748·01	1217	12·04	9·88
16	13·63	746·37	1205	13·59	11·28
18	15·48	744·52	1192	15·32	12·84
20	17·54	742·46	1178	17·24	14·61

It will be seen that : (*a*) the amount of water vapour in 1 cubic metre of saturated air increases as the temperature rises ; (*b*) the quantity of water vapour carried by 1 kgm. of dry air increases even more rapidly.

Air containing the maximum possible amount of water vapour at any particular temperature is said to be *saturated* with water vapour at that temperature. Thus at 20° C. a cubic metre of saturated air contains 17·24 gm. of water vapour, whilst at 10° C. it contains only 9·39 gm. of water vapour. If, therefore, a cubic metre of saturated air at 20° C. be cooled to 10° C., there will be a deposition of water vapour.*

The atmosphere is not normally saturated with water vapour, and when unsaturated air is cooled, no moisture is deposited until the air passes the *saturation point*. The temperature at which this condensation of moisture occurs is termed the *dew point*. When a mass of moist air has its

* To calculate the amount of deposition we proceed as follows : A cubic metre of saturated air at 20° C. contains 17·24 gm. of water vapour and 1178 gm. of air. This air is not condensed, of course, and will go to form $\frac{1178}{1236}$ cubic metres of saturated air at 10° C., and this quantity of air will hold $\frac{1178}{1236} \times 9{\cdot}39 = 8{\cdot}96$ gm. of water vapour. The quantity deposited will therefore be $17{\cdot}24 - 8{\cdot}96 = 8{\cdot}28$ gm. of water vapour. Owing to the contraction of the air on cooling, it is impossible to perform this calculation by finding the difference in water vapour content at the two different temperatures.

temperature lowered, either by being forced to rise to higher colder regions or by meeting another mass of colder air, rainfall occurs. The temperature is lowered until the saturation point is reached, when deposition occurs. Minute water droplets are formed which coalesce to form larger drops which fall to earth.

The *relative humidity* of the atmosphere under any conditions is defined as the ratio between the pressure of the water vapour in the air under those conditions and the saturation vapour pressure under the same conditions.*

The methods of determining the moisture in the atmosphere at any given time may be grouped as follows: (*a*) the chemical method; (*b*) physical methods.

(*a*) The *chemical method* is an absolute one, and actually determines the amount of water vapour present in a given quantity of air. It is rarely used in routine work; the operations required are far too lengthy. Briefly, it consists

* There are three methods of defining relative humidity, all of which give different results (except at 0 % and 100 %). These are:

(*a*) $\text{R.H.} = \dfrac{\text{pressure of water vapour actually present}}{\text{saturation pressure}}$

(*b*) $\text{R.H.} = \dfrac{\text{wt. of water vapour actually present per unit volume moist air}}{\text{wt. of water vapour present in unit volume saturated air}}$

(*c*) $\text{R.H.} = \dfrac{\text{wt. of water vapour actually present per kgm. dry air}}{\text{wt. of water vapour required to saturate 1 kgm. dry air}}$

(*a*) is the definition quoted in the text and is the one usually employed in elementary physics.

(*c*) is the logical definition, since mass units are independent of temperature and pressure. This definition simplifies calculations on humidification or air conditioning. To illustrate the differences in these three methods, consider the following conditions. Air temp. 20° C. Dew point 10° C.

(*a*) $\text{R.H.} = \dfrac{\text{saturation pressure at } 10^\circ \text{ C.}}{\text{,, ,, } 20^\circ \text{ C.}} = \dfrac{9{\cdot}21}{17{\cdot}54} = 52{\cdot}5\ \%$

(*b*) $\text{R.H.} = \dfrac{\text{wt. water vapour in 1 cubic metre of saturated air at } 10^\circ \text{ C.}}{\text{,, ,, ,, ,, ,, ,, } 20^\circ \text{ C.}}$

$$= \frac{9{\cdot}39}{17{\cdot}24} = 54{\cdot}5\ \%$$

(*c*) $\text{R.H.} = \dfrac{\text{wt. of water vapour required to saturate 1 kgm. dry air at } 10^\circ \text{ C.}}{\text{,, ,, ,, ,, ,, ,, ,, } 20^\circ \text{ C.}}$

$$= \frac{7{\cdot}59}{14{\cdot}61} = 51{\cdot}9\ \%$$

in slowly passing a known volume of air through a series of weighed tubes containing chemical reagents to absorb water vapour (calcium chloride or phosphorus pentoxide are usually used). The increase in weight of the tubes, after the passage of the air gives the quantity of water vapour absorbed.

(*b*) The *physical methods* can be divided into two groups; those involving a determination of the dew point, and the wet and dry bulb hygrometer.

The Determination of the Dew Point. The dew point is the temperature at which the water vapour present in the air is sufficient to saturate it. For instance, if the air temperature be 20° C. and the dew point 12° C., then the pressure of aqueous vapour at the dew point * = 10·52 mm., and the pressure of aqueous vapour necessary for saturation at 20° C. = 17·54 mm.

$$\text{Hence the relative humidity} = \frac{10{\cdot}52}{17{\cdot}54} = {\cdot}6, \text{ i.e. 60 per cent.}$$

This means that the air contains 60 per cent of the maximum possible amount of water vapour. The dew point can be determined in the following ways :

Regnault's Hygrometer. This consists of a boiling tube fitted with an outer silver polished thimble. The cork of the tube carries a thermometer and glass delivery tube (Fig. 32). A small quantity of ether is placed in the tube and a rapid stream of air is drawn through it by means of an aspirator. The rapid stream of air evaporates the ether ; the latent heat required for the evaporation being taken from the surrounding air, the tube, and thimble. Thus the air in the immediate neighbourhood becomes cooled until it reaches a temperature at which the air is saturated with water vapour ; any further fall in temperature results in a deposition of moisture in the form of dew on the silver thimble. The latter is highly polished in order to render easier the observation of the production of the dew. The temperature indicated on the thermometer immersed in the ether gives the dew point, and a thermometer hanging in the air gives the air temperature.

A more accurate determination of the dew point can be made by allowing the apparatus to warm up and observing the temperature at which the dew disappears. The average

* Found from tables, see p. 104.

of the two dew points is then employed for the calculation of relative humidity.

Daniell's Hygrometer. This instrument depends for its use on the same principle as the Regnault hygrometer, i.e. evaporation of ether to cool air to the dew point.

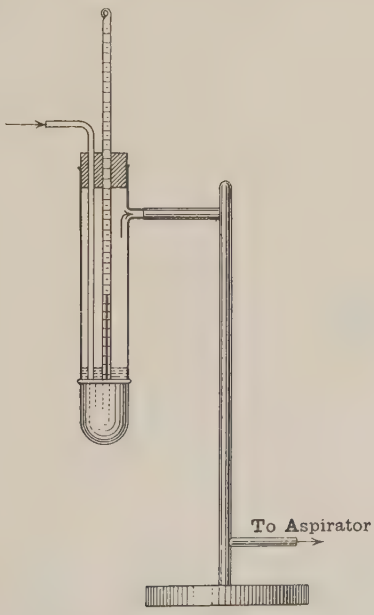


FIG. 32.—REGNAULT'S HYGROMETER

It consists of two glass bulbs connected by wide glass tubing, arranged as in sketch. Each bulb contains some ether which by tipping the apparatus may be passed completely into either bulb. The right-hand bulb (Fig. 33) has a piece of muslin wrapped round it and is cooled by the evaporation of ether poured over it. Then, since the temperature in this bulb is less than in A, ether commences to evaporate from A. Thus the temperature in A falls, and the air surrounding it is

cooled until dew is just deposited on a polished gold band painted on the bulb. The dew point is indicated by the temperature on a thermometer fitted inside bulb A, and the air temperature by a thermometer hanging near the instrument. The relative humidity can be determined exactly as described on page 106.

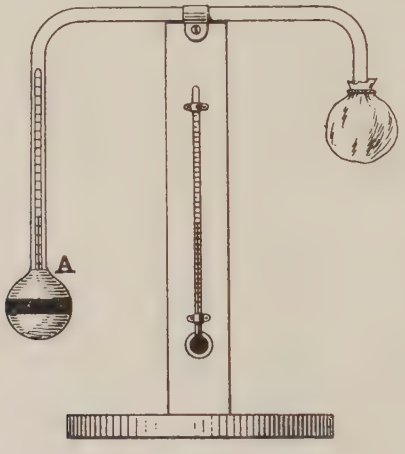


FIG. 33.—DANIELL'S HYGROMETER

Wet and Dry Bulb Hygrometer. The commonest method of determining humidity is by means of an instrument termed the "Wet and Dry Bulb Hygrometer." Two similar thermometers hang side by side, the bulb of one being wrapped in a piece of muslin kept constantly wet by dipping into a small bottle of water below it. The dry thermometer measures the prevailing air temperature. Suppose the air is dry or contains very little moisture, then moisture tends to evaporate from the wet muslin into the air. The extent to which this happens will depend on the amount of moisture already in the air. Evaporation from the wet muslin requires heat, which is taken from the bulb of the thermometer, i.e. the wet thermometer will register a lower temperature than the dry one. Thus the drier the air the more moisture will evaporate from

the wet thermometer, and the greater will be the divergence or difference in the readings of the two thermometers. If the air were saturated with water vapour, then obviously no more would evaporate from the wet muslin, and the two thermometers would read the same temperature. Thus the difference in the readings of the two thermometers is an index or a measure of the " dryness " of the atmosphere. The greater the difference the drier is the air, and the nearer the two readings are, the closer does the air approach to complete saturation.

The actual relation between the difference in the readings of the two thermometers for any particular reading of the dry thermometer has been accurately worked out and the result embodied in a complicated formula from which Hygrometric Tables have been made. These tables are usually supplied with the instrument.

This method of determining the relative humidity is largely employed, owing to the ease of determination. It is only necessary to read two temperatures and use the tables, though it should be noted that mere observation of a hanging instrument generally gives erroneous results. It has been recommended that the instrument be passed backwards and forwards rapidly in the air or swung round and round, in order to provide the fullest possible opportunity for water to evaporate from the wet bulb. This procedure is highly necessary for accurate observation.

Effect on Variation of Humidity on Milling Operations. The question of the relative humidity of the atmosphere and its variation is of some importance to millers, since variation may affect their products or even interfere with the actual milling operations. Many millers must have observed that on a damp day, when the humidity is high, the stocks do not run freely and are liable to choke in the spouts, likewise they do not pass through the silk in the dressers readily, even the silk itself expands and contracts with changes in humidity. Further, " sweating " on the rolls and inside the milling machines is due to the fact that the air inside the machine has become saturated with water vapour probably by evaporation of water from the stocks passing through the rolls. Any lowering of the temperature of the air in the machine, due to

a draught of cold air or a cold surface, will cause deposition of moisture.

Some of these difficulties are largely due to the fact that flour is *hygroscopic* in nature, i.e. it is able to absorb or lose moisture from or to the atmosphere according to the humidity of the atmosphere. If there be much moisture in the air, then the flour will absorb some till a balance is reached. If there is little moisture in the air, then the flour will lose some to it till again a balance is reached. The percentage of moisture to be found in flour is more or less dependent on the humidity of the atmosphere, and it has been shown that percentage moisture in a sample of flour exposed to the air varies from day to day as the humidity changes.

In order to overcome difficulties in a mill arising out of the variation in humidity, some mills artificially control the humidity by the injection of moisture-laden air into the atmosphere when required. Such control needs of course necessarily go hand in hand with judicious ventilation of the mill, otherwise the air of carefully regulated humidity may be lost.

It is a common thing in the cotton mills in Lancashire to control the humidity to a value found to be the best for the successful manipulation of the cotton. Air conditioning in flour mills is a common thing in the United States, where considerable temperature and humidity changes constantly occur; temperatures may vary from 82° F. to 27° F. and humidity from 40 per cent to 100 per cent. In mills where air conditioning is practised, it is claimed that variations in humidity do not exceed 4 per cent.*

Effect of Variations in Atmospheric Humidity on the Moisture Content of Wheat and Flour. It is well known that wheat and flour are hygroscopic, i.e. they absorb more or less moisture from the atmosphere according to the humidity of the latter.

It has been observed with American wheats that the average moisture contents of samples reaching the mills gradually rose during the winter months (September–March) and fell during the drier warmer summer months. Similar observations have been made by Dr. A. E. Humphries over a

* For further information see *Milling*, July 7, 1928.

period of years. From a survey of the moisture contents of samples of English wheat reaching the Coxes Lock Mill, Weybridge, it has been observed that there is a rise in the average moisture content during the winter months and a subsequent fall in moisture content, due to the rising temperature and falling atmospheric humidity of the spring and summer. The variations in the case of flour have also been investigated by Dr. A. E. Humphries. The moisture content of a sample of flour which had been allowed to dry at 90° F. was determined; 5 gm. of the material was then freely exposed to atmospheric conditions in a shallow aluminium dish placed in a ventilated box free from draughts. The dish and contents were weighed each morning and the humidity of the atmosphere was also recorded. The following were some of the results obtained.

Date	*Moisture present per 100 gm. sample*	*Relative Humidity of the atmosphere*
June 8	8·80 gm.	62
„ 9	15·02 „	78
„ 10	15·10 „	69
„ 11	14·28 „	—
„ 12	16·16 „	82
„ 13	17·00 „	—
„ 15	16·99 „	75
„ 16	16·26 „	78
„ 17	15·56 „	69
„ 18	15·51 „	80
„ 19	16·27 „	91
„ 20	17·85 „	83
„ 22	15·45 „	72
„ 23	15·54 „	74
„ 24	15·68 „	62
„ 25	15·48 „	80
„ 26	14·64 „	70
„ 27	14·68 „	76·5
„ 29	14·43 „	63
„ 30	12·20 „	59

These results have been plotted to form a graph, Fig. 34,

which shows how closely the moisture content of the flour follows the humidity of the atmosphere.

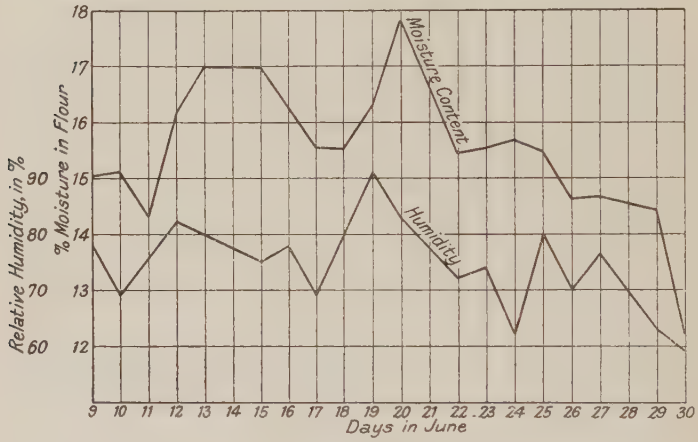


FIG. 34

CHAPTER X

MAGNETISM AND ELECTRICITY

THE phenomenon of magnetism is displayed principally by the metal iron. Iron, if treated in a particular manner, acquires the property of attracting to it other pieces of iron ; the iron is said to be *magnetic* or to behave as a *magnet*. There are various ways by which a piece of iron may be rendered magnetic.

(1) By gentle rubbing in a particular way with a piece of iron already magnetic. Such treatment renders the iron a permanent magnet, i.e. the specimen remains magnetic when the magnetising influence is removed.

(2) By winding a coil of wire round the specimen and passing an electric current through the wire. When the current is passing, the iron rod behaves as a magnet, but the greater part of its attractive power vanishes when the current

is turned off. Such an arrangement is termed an *electro-magnet*; electro-magnets are far more powerful than ordinary permanent magnets.

Magnets are commonly made in two shapes: (*a*) a straight bar, or "bar" magnet; (*b*) bent in the shape of a horseshoe, a "horse-shoe" magnet. If a bar magnet be suspended about its centre so that it is free to rotate in a horizontal plane, it will be found that the magnet will come to rest in a definite direction, viz. with one end pointing towards the north and the other to the south. The former end of the magnet is termed the north-seeking pole, and the latter the south-seeking pole. For convenience, these will be termed simply "north" or "south" poles respectively. It is one of the fundamental laws of magnetism that "like poles repel each other and unlike poles attract each other." The earth itself acts as a magnet with one pole termed the "north magnetic pole," not far removed from the geographical north pole, and the other pole, the "south magnetic pole," in close proximity to the geographical south pole.

The attraction and repulsion between unlike and like poles can readily be shown by suspending a magnet by a thread and bringing near to its south pole the north pole of a second magnet; attraction between the two poles results. If instead of a north, a south pole be brought near, then repulsion occurs. A magnet exerts an influence in the space immediately surrounding it, and the zone of influence of the magnet is termed the *magnetic field* of the magnet.

The *field* can be "mapped," i.e. an idea of the direction of the magnetic forces acting in the field can be discovered by sprinkling iron filings on a sheet of paper under which is placed a magnet. If a small magnetic needle were placed in this magnetic field it would set in a direction indicated by these *lines of magnetic force*.

Map of Magnetic Field. Fig. 35 shows the magnetic field about a single bar magnet. Fig. 36 (*a*) and (*b*) the fields about a north and south pole and about two north poles respectively. Note the repulsion and low magnetic intensity immediately between the poles in Fig. 36 (*b*) and the attraction and high magnetic intensity between the poles in Fig. 36 (*a*).

Fig. 37 shows the magnetic field due to a horse-shoe magnet. It is found that the magnetic intensity is greatest nearer the

poles and that the lines of force tend to curve round from a north to a south pole. The lines of force from unlike poles tend to turn away from one another.

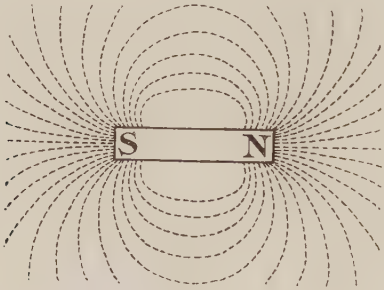
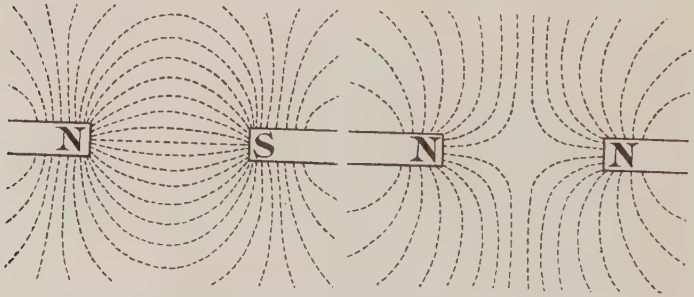


FIG. 35

The Electro Magnet. An electro-magnet may be made by passing an electric current through a coil of wire surrounding either a bar of iron or a piece of iron shaped as a horse-shoe.



(*a*) (*b*)

FIG. 36

The iron will be rendered magnetic and the end at which the current is passing round the specimen in an anti-clockwise direction becomes the north pole of the magnet.

Such electro-magnets and also ordinary permanent bar

magnets are employed in flour mills to remove nails, pieces of iron, etc., from dirty wheat. The wheat passes down a

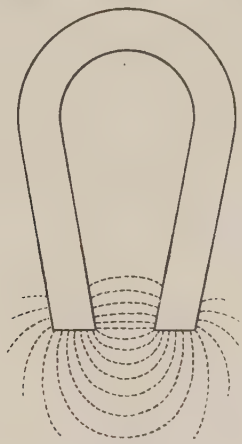


FIG. 37

chute and over the poles of the magnet. The latter attract and hold any iron particles which may be present, and these

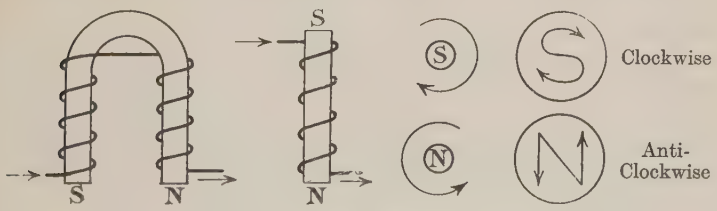
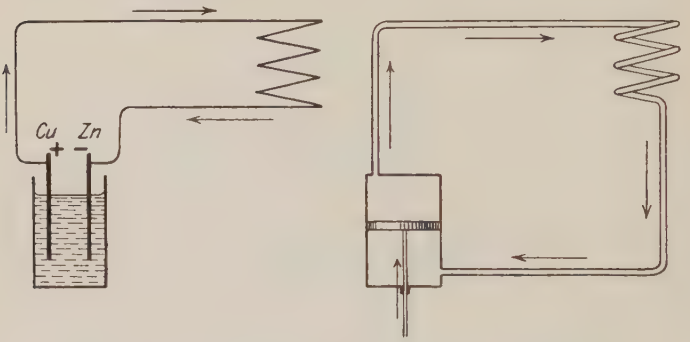


FIG. 38

are removed from time to time by hand from the poles of the magnet.

Electricity. If a plate of copper and of zinc be immersed in a solution of dilute sulphuric acid, and the plates be connected by a copper wire outside the cell, it is found that a current of electricity passes along the wire from the copper to

the zinc. Such an arrangement is termed a *simple voltaic cell* (after Volta, an Italian physicist, who devised a similar arrangement in 1800). The causes underlying the generation of this electric current are beyond the scope of this volume. The fact that the copper wire is behaving in an apparently peculiar way may be demonstrated by the fact that a magnetic field is set up around the wire. The copper wire is acting as a conductor of electricity. The apparent movement of electricity that is involved can perhaps be imagined by comparing the arrangements of a simple voltaic cell to a plunger forcing water through a pipe system. Upward movement of the plunger (Fig. 39*a*) forces water out of the cylinder at the



(*a*) FIG. 39 (*b*)

top, through the circuit and back into the cylinder at the bottom. The greater the force applied on the plunger the greater will be the *rate* at which water flows round the circuit. Thus the rate of flow of water will depend on the difference in pressure set up on the upper and lower sides of the plunger. The energy resulting from the chemical action of the zinc and copper and the sulphuric acid is sent out along the connecting wire in the form of electrical energy, i.e. a current flows along the wire.

It is convenient to consider that this flow is caused by some difference of electrical pressure analogous to the difference of pressure in the case of the water piston. This difference of electrical pressure causing the flow of electricity is

termed a *difference of potential.* Potential difference is commonly measured in volts and represents the force with which an electric current is driven round a circuit. It is also referred to as the *electro-motive force* or E.M.F. of the cell. The value of this E.M.F. depends on the type of cell considered, but for simple primary voltaic cells it is about 1 to 2 volts.

Considering again the water circuit in Fig. 39 (*b*). For any given pressure the water circulation will depend on the length and diameter of pipe the water has to be forced through. With short, wide pipes much water will pass, whilst with long, narrow pipes much less water will pass. Similar features are observed with a voltaic cell. Provided the connecting copper wire is short and thick, a high current will pass, but if a long wire be used or wire of narrow cross section, then the current will be much diminished.

Thus it will be seen the current furnished by any given cell will depend upon the metallic conductors composing the circuit through which the current passes. The strength of current is measured in units termed *amperes.**

The greater the resistance offered by a wire to the passage of an electric current, the less current will flow for any given potential difference. The current strength, potential difference, and the resistance of a conductor are connected by *Ohm's Law*, which states that " provided the temperature of a conductor be kept constant, the ratio of the P.D. between any two points to the current strength is constant," or expressed in symbols :

$$\frac{E}{I} = \text{constant} = R,$$

where E = the potential difference,

I = the current strength,

R = a constant which is termed the " resistance " of the portion of material under consideration.

The unit employed in measuring resistance is termed the

* The " ampere " is defined as that current strength which, if passed through a solution of silver nitrate, will cause the deposition of 0·001118 gm. of silver every second.

ohm,* and the practical unit of potential difference is the *volt*.†

Examples illustrating Ohm's Law. What should be the resistance of an electro-magnet winding if it is required to use 1·4 amperes through the magnet, and a direct current supply of 110 volts is available ?

$$\frac{E}{I} = R, \text{ i.e. } \frac{\text{E.M.F.}}{\text{current strength}} = \text{resistance},$$

$$\therefore \quad \frac{110}{1{\cdot}4} = 78{\cdot}5 \text{ ohms} = \text{resistance}.$$

In addition to the units already mentioned, the following are in common use :

The Unit of Quantity of Electricity. This is the *coulomb*, defined as the quantity of current which has passed a given point in a conductor when a current of one ampere has been flowing for one second.

The Unit of Electrical Power. This is the *watt*, defined as the power developed when one volt forces a current of one ampere round a circuit, i.e.

Power in watts = current in amps. × E.M.F. in volts.

The *kilowatt* represents 1,000 watts, approximately equal to $1\frac{1}{3}$ horse-power, and the *kilowatt hour* (a unit of electrical energy) represents the energy expended when 1 kilowatt is exerted for one hour. This is the unit by which electrical energy is bought and sold, also called B.O.T. Unit (Board of Trade Unit).

Effects of an Electric Current. The presence of a current of electricity in a wire can be detected by the effects it produces. The most important are : (1) the magnetic effects, (2) the chemical effects, (3) the heating effects.

Magnetic Effect of an Electric Current. If a coil of insulated wire be wound round a bar of iron and a current is passed round the coil, the bar becomes a " magnet," and has the

* The ohm is defined as being the resistance of a column of mercury 106·3 centimetres long, 1 square millimetre in cross section at 0° C.

† The volt is defined as that potential difference of electrical pressure which, if applied steadily to a conductor whose resistance is one ohm, will produce in it a steady current of one ampere.

power of attracting other pieces of iron to it. With ordinary soft iron the bulk of the magnetic properties vanish when the current is switched off, but with a bar of hard steel much of the magnetism remains after removal from the coil and the bar can be used as a permanent magnet. The magnetic effect of an electric current is employed in electric bells, many telegraph and telephone instruments, electro-magnets, electric motors and dynamos.

Progress during the second half of the nineteenth century was due largely to the introduction of the dynamo, telegraph and telephone. The dynamo is a machine for converting mechanical energy into electrical energy. Before the introduction of the dynamo, electrical energy was derived from voltaic batteries, a costly source. For the invention of the

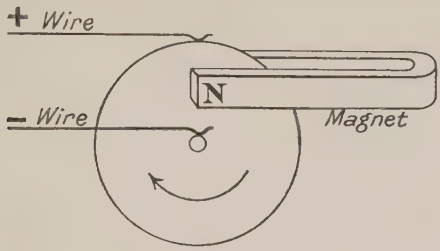


FIG. 40

dynamo, we are indebted to Michael Faraday, who from his experiments on *induced electric currents* first devised a simple dynamo in 1831. He observed that if the lines of force between the poles of a magnet be cut by a metallic conductor an electric current is set flowing in the conductor. The current is said to be *induced* in the conductor, as a result of the cutting or intersecting of the lines of force constituting the magnetic field of the magnet.

The first simple experiments were carried out with a metal disc mounted so that it could be rotated edgewise between the poles of a permanent horse-shoe magnet (Fig. 40). When rotated, the disc cuts the lines of force which intersect its upper half, and by connecting two rubbing contacts, one on the circumference and the other on the spindle, Faraday showed that a continuous current could be produced so long

as the disc was rotated. Thus the two essential parts of a dynamo are the magnet, to provide the necessary lines of force, and the electrical conductors represented in Faraday's original experiment by the metal disc.

With the development of the dynamo the disc was replaced by many wires wound in such a way as to add up their several E.M.Fs. The wires are usually wound on an iron structure, the whole being referred to as the *armature* of the dynamo. In modern dynamos the armature may either rotate between the poles of the magnet or in some the magnet rotates whilst the armature is stationary. In the construction of modern dynamos the aim is to so dispose the conductors and magnetic field as to produce maximum cutting of the magnetic lines. Since also the E.M.F. produced is proportional to the rate of cutting of lines, the rotational speed is important. With

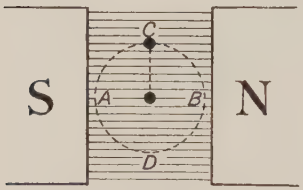


FIG. 41

A B Positions of maximum cutting of lines of force.
C D Positions of minimum cutting of lines of force.

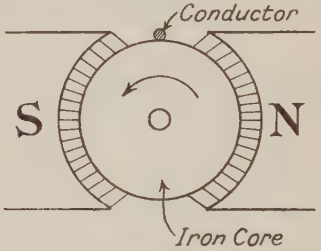


FIG. 42

parallel pole pieces and an armature composed of a single wire loop (Fig. 41), the direction of movement is not always at right angles to the direction of the magnetic lines which pass straight across from the two faces. The result is that the E.M.F. rises to a maximum and falls away again to zero every half revolution. Also since the direction of line-cutting changes each half revolution, the E.M.F. changes direction every half revolution. If the ends of the wire loop be connected to two collecting rings, insulated from the spindle and from which sliding contacts termed " brushes " collect the current, an " alternating " current will flow when the circuit is completed, i.e. one whose direction reverses at a rate according to the rate of revolution. If shaped pole-pieces be

employed and the conductor be mounted on an iron core, the direction of movement becomes almost all at right angles to the lines of force (Fig. 42), and a steadier though still alternating current is obtained.

If the ends of a conductor be connected to a split tube of copper, which rotates with the conductor, *direct current* is produced. Brushes rubbing against the tube collect the current and convey it to the circuit. Such a split-ring device is an elementary form of *commutator* used to convert the alternating current produced in the coil to a direct current in the circuit. If the coil be rotating in a clockwise direction

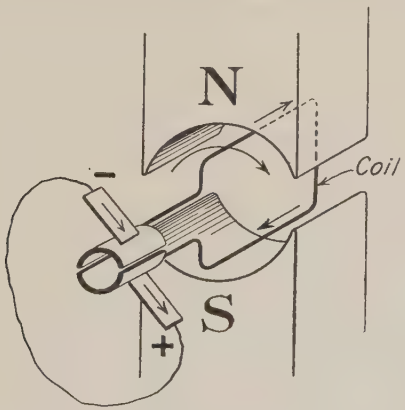


FIG. 43

an E.M.F. will be produced in the coil in the direction of the arrows (Fig. 43), the upper brush being negative and the lower positive. After one half rotation, when the direction of line cutting reverses, the E.M.F. flows in the coil in the reverse direction, tending to make the split ring, which *was* negative, positive. But by the time this phenomenon occurs, the split ring has made one half rotation and is now in contact with the lower positive brush. Thus the upper brush remains always negative and the lower always positive and a direct current flows in the circuit connecting the brushes.

Chemical Effect of an Electric Current. If an electric

current be passed through water acidulated with dilute sulphuric acid, it is found that the water is decomposed into its constituents, namely oxygen and hydrogen.

Oxygen gas is liberated at the positive pole, where the current enters the water, and hydrogen is liberated at the negative pole :

$$2H_2O = 2H_2 + O_2$$

The water is termed an *electrolyte*, i.e. a conductor of electricity which undergoes decomposition by the passage of the current. Under the influence of the P.D. applied the electrolyte decomposes, and the constituent portions tend to move in opposite directions and are liberated at the poles or electrodes. The particles which actually carry the current are termed *ions*, i.e. hydrogen ions or positively charged hydrogen particles move towards the negative pole where their charge becomes neutralised and the hydrogen appears as ordinary gaseous hydrogen. Similarly with the oxygen. The decomposition of a substance in solution by an electric current is referred to as *electrolysis*.

Chlorine is now made on a commercial scale by the electrolysis of a solution of common salt. The solution contains sodium ions and chlorine ions which under the influence of the current are directed towards the negative and positive poles respectively, where their charges are neutralised and ordinary sodium and chlorine appear. The sodium, however, immediately reacts with the water, forming hydrogen and caustic soda :

$$2Na + 2H_2O = 2NaOH + H_2$$

The net result of the electrolysis of a solution of common salt is :

(*a*) chlorine liberated at the positive pole,
(*b*) hydrogen ,, ,, the negative pole,
(*c*) sodium hydroxide accumulates in the solution around the negative pole.

The chlorine is stored under pressure in cylinders and the caustic soda is obtained from the resulting liquors by evaporation. Silver nitrate also decomposes when subjected to electrolysis and metallic silver is liberated at the negative pole. The quantity of silver deposited per second is a measure of the current strength. (See definition of " ampere.")

Heating Effect of an Electric Current. When an electric current is passed through a wire, the wire becomes heated, i.e. electrical energy is being converted to heat energy. The quantity of heat developed and the temperature attained depend on a number of factors. Briefly the relationship is expressed by the following formula :

$$H \propto C^2Rt, *$$

where H = heat developed in calories,
C = current passing in amperes,
R = resistance in ohms,
t = time in seconds,

or the expression can be written :

$$H \propto \frac{E^2}{R}t,$$

where E = the E.M.F.

Thus if part of a circuit consists of a thin tungsten wire, the wire may get so hot as to give out light. This fact is employed in electric lamps. The heating effect of an electric current is also used in electric furnaces, ovens, fires and domestic irons, electrical fuses, etc. Each depends for its use on the heat developed when a current is passed through a thin wire.

In the case of electrical fuses, at a certain point in a circuit is placed a short length of thin wire of fairly low melting point, usually an alloy of lead and tin. This acts as a safety device since if the current in the circuit rises beyond a certain value, so much heat is developed in the fuse that it melts and breaks the circuit. This protects the remainder of the circuit from overheating, and also since the fuse is placed in a specially designed compartment in a position easy of access, it is a comparatively simple matter to repair the circuit by refitting a fresh piece of fuse wire.

* $\propto$ = is proportional to.

APPENDIX TO PART I

COMMON TERMS EMPLOYED IN CHEMISTRY

Combustion. A term used to indicate a chemical reaction usually accompanied by the appearance of flame ; commonly referred to as " burning." When a substance burns in air it combines with oxygen of the air. This chemical combination is accompanied by an evolution of heat. The heat is given out rapidly and is sufficient to raise the temperature of the products to incandescence, i.e. they glow and give out light ; in other words " flame " is produced. Such changes occur when, say, carbon unites with oxygen rapidly ; for every gram of carbon burnt, a definite quantity of heat is given out (the " Heat of Combustion ").

If the combination takes place slowly, then the evolution of heat takes place over a period of time. During this time the heat is lost from the substance by various means and an elevated temperature is not reached. Hence no flame is produced. But exactly the same heat evolution per gram of carbon is attained as when flame is produced. Such flameless combustions take place in the human body, where the waste tissues are oxidised (i.e. combine with oxygen) by the oxygen in the blood stream and the evolution of heat maintains body temperature. These flameless combustions may be referred to as slow " oxidations " or slow " combustions " as compared with rapid oxidation or rapid combustion, usually referred to as " burning." Super-rapid oxidations or combustions are termed explosions.

Oxidation may be described generally as a process of combination with oxygen. Thus carbon is oxidised to carbon dioxide when it is burnt. Likewise compounds may be oxidised to other compounds of greater oxygen content. Possibly during the bleaching or ageing of flour the colouring matter (called " carotin ") becomes " oxidised " to some compound of greater oxygen content, which is colourless.

Further examples of this type of oxidation :

$$\underset{\text{carbon monoxide}}{2CO} + O_2 = \underset{\text{carbon dioxide}}{2CO_2}$$

$$\underset{\text{Sulphur dioxide}}{2SO_2} + O_2 = \underset{\text{Sulphur trioxide}}{2SO_3} \text{ (in the presence of a catalyst)}$$

A process whereby a compound loses the element hydrogen is also described as an oxidation, e.g. hydrochloric acid may be oxidised to chlorine :

$$4HCl + O_2 = 2H_2O + 2Cl_2$$

This change may be brought about in a variety of ways, the reagent supplying the necessary oxygen being termed the " oxidising agent." Thus if hydrochloric acid be heated with manganese dioxide (MnO_2), potassium permanganate (K^1MnO_4), or potassium dichromate ($K_2Cr_2O_7$), chlorine is produced. Under some conditions oxygen from the air may be employed. These reagents which supply the oxygen are termed oxidising agents.

A certain number of other reactions involving no oxygen or hydrogen change are also termed oxidations, e.g. the conversion of a compound of an element of lower valency to one of higher valency (ferrous chloride to ferric chloride).

Reduction is a process involving generally a loss of oxygen from, or addition of hydrogen to, a compound or element. The agent affecting the reduction is usually some substance with a great affinity for oxygen, e.g. hydrogen, carbon, or carbon monoxide.

Thus, in the manufacture of iron, the oxide of iron is reduced by means of carbon or carbon monoxide :

$$Fe_2O_3 + 3C = 2Fe + 3CO$$
$$Fe_2O_3 + 3CO = 2Fe + 3CO_2$$

Hydrolysis. A term used to indicate the partial decomposition which nearly all salts undergo with water. The extent of the hydrolysis depends on the nature of the parent acid and base constituting the salt. A salt of a strong base and acid is practically unaffected by water, e.g. sodium chloride NaCl, whilst salts of strong bases (like NaOH, KOH) with weak acids (like carbonic acid H_2CO_3) react alkaline to indicators owing to the preponderating effect of the base over that of the acid :

$$Na_2CO_3 + 2H_2O \rightleftharpoons 2NaOH + H_2CO_3$$

On the other hand salts of weak bases with strong acids often react acid to indicators. The term " hydrolysis " is often employed in organic chemistry to indicate another type of change, viz. the decomposition of a complex substance usually in the presence of a catalyst to produce two simpler substances, e g. the hydrolysis of cane sugar to glucose and fructose by boiling with water in the presence of a small quantity of sulphuric acid. (See Part II, p. 156.)

Electrolysis. A decomposition of a chemical compound by

means of an electric current. Electrolysis may occur in the aqueous solution of a compound (usually a salt) or in the molten or liquid state, e.g. when an electric current is passed through slightly acidulated water, decomposition of the water occurs. No decomposition occurs if the water be perfectly pure. This is attributed to the lack of *ions* in the pure water, but the number of these is increased by the presence of the sulphuric acid. Ions may be regarded as charged particles existing in the liquid which carry the current from one pole to the other. Without these no passage of current takes place, the liquid is a non-conductor of electricity and is termed a " non-electrolyte," e.g. paraffin oil is a non-electrolyte. Most salts when dissolved in water give rise to " ions," and the solutions conduct electricity ; these are termed electrolytes.

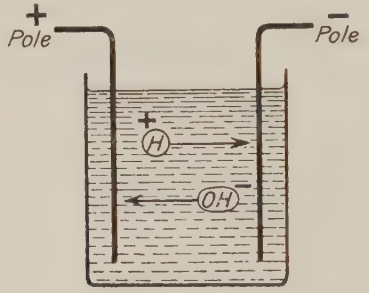


FIG. 44

When an electric current is passed through acidulated water the hydrogen ions carry a positive charge of electricity from the positive to the negative pole. Here the charge is neutralised by the charge on the plate and the hydrogen appears as ordinary gaseous hydrogen. The OH, or hydroxyl ions, carry a negative charge from the negative to the positive plate where the charges become neutralised, and two OH groups react to form water and ordinary gaseous oxygen which is liberated. Thus the net result of the electrolysis is the evolution of hydrogen at the negative pole and oxygen at the positive pole. Two volumes of hydrogen are produced for every one volume of oxygen :

$$H_2O \rightleftharpoons H^+ + OH^-$$

When common salt (sodium chloride NaCl) is dissolved in water it immediately " ionises " to yield Na^+ ions and Cl^- ions. On applying a current of electricity, the Na ions travel towards the negative pole where the charges becomes neutralised, atomic

sodium appears but immediately reacts with the water forming hydrogen and sodium hydroxide, according to the equation :

$$2Na + 2H_2O = 2NaOH + H_2$$

The chlorine ion likewise travels toward the positive pole and is liberated as gaseous chlorine.

This method is employed for preparation of chlorine industrially. The products from the two poles are kept separated by a porous partition to avoid interaction between the chlorine and the sodium hydroxide formed. (See also hydrogen ion concentration : Appendix, Part II).

Catalysis is a process in which the rate at which two chemical compounds react is influenced (usually increased) by the presence of a small quantity of a third substance. The final products are the same whether the catalyst be used or not ; it is only the rate at which the reaction proceeds or the time taken to reach the final stage that is affected, e.g. in the exothermic process for the production of nitrogen peroxide for the bleaching of flour, ammonia is oxidised in the presence of a catalyst to nitrogen peroxide and water according to the equation :

$$4NH_3 + 7O_2 = 4NO_2 + 6H_2O + x \text{ calories}$$

The oxygen necessary is supplied by the air. This change occurs without a catalyst but at such an extremely slow rate as to be almost unobservable. If, however, the ammonia and air in the required proportions be passed over a red-hot platinum wire, then the oxidation takes place rapidly. The platinum acts as a catalyst ; it remains unchanged after the reaction and behaves in a way as a kind of " stimulant " to the reaction. The action of a catalyst has been compared to that of a whip upon a horse.

Synthesis, a process of building up a compound from its elements, e.g. water can be synthesised by combining oxygen and hydrogen. Many naturally occurring compounds have been synthesised in the laboratory.

Photo-synthesis is a process of building up a compound from carbon dioxide and water by a plant during its growth. Plants take in carbon dioxide through the leaves and water from the soil ; under the influence of sunlight and in the presence of " chlorophyll," the green colouring matter of plants, the carbon dioxide and water are built up into such compounds as starch and sugar.

Analysis is a process of decomposition of a compound with a view to ascertaining either the nature or quantity of the constituent elements. The former is termed " Qualitative " and the latter " Quantitative " analysis. In qualitative analysis the elements themselves are not isolated but properties characteristic of them are looked for in the compound to be analysed.

EXAMINATION PAPERS OF THE CITY AND GUILDS OF LONDON INSTITUTE TECHNOLOGICAL EXAMINATIONS.

Flour Milling, Intermediate Course, 2nd year.

1927.

1. What is meant by the term "density"? Show how advantage is taken of different densities in order to effect separation in milling.

2. What is "specific heat"? Given that the specific heat of flour is 0·42, what should be the temperature of 14 gallons of water used to make dough at 82° F. with 280 lbs. flour at 70° F.? (1 gallon of water weigh 10 lbs.)

3. What is "vapour pressure"? Explain evaporative loss and sweating by means of vapour pressure.

4. Define an "ampere," and "electro-motive force." What is "Ohm's Law"? An electric lamp takes a current of 0·7 amperes and the E.M.F. between its terminals is found to be 98 volts. What is its resistance?

5. What is the difference between a chemical compound and a physical mixture? Give examples.

6. How is chlorine prepared? What are its properties and uses?

7. Show how NO_2 can be obtained direct from the air or from ammonia. What are its properties and uses?

8. How many oxides of carbon are known? Name them and show how important one of them is to the miller and baker.

1928.

1. Supposing that a well gives a plentiful supply of water without appreciable change in water-level in the well and that the water-level stands at 45 feet below the surface, where would you place the pump and why? How is this question connected with barometric pressure?

2. On what principle does the thermometer depend ? Explain the instrument in detail and state why mercury is usually used.

3. Describe both forms of magnet—electro and permanent. State the advantages and disadvantages of both. Supposing you had a direct current supply at 110 volts and you wish to use 1·4 amperes, what should be the resistance of the windings of your electro-magnet ?

4. Of what use is the " Hygrometer " in milling ? How does it differ from the " Hydrometer " ? On two successive days the wet and dry bulbs read :

	Wet.	*Dry.*
1.	65° F.	65° F.
2.	63·5 F.	65° F.*

Which was the drier day ?

5. What are the principal elements present in coal ? Describe the combustion changes which take place in a boiler furnace.

6. What easy test would you use to distinguish lime water ? How would you redissolve the precipitate ?

7. What are the distinguishing features of acids ? Name the common acids and those associated with flour.

8. How would you prepare NaOH, HCl, NaCl ? How much common salt can be obtained when 1 lb. of NaOH is added to hydrochloric acid ?

Atomic Weight Na = 23.
,, ,, Cl = 35·5.

1929.

1. What is meant by expansion of solids ? Show the importance of understanding this phenomenon in setting a roll. Show also how expansion of liquids is utilised for measuring temperature.

2. Explain how a syphon works and why.

3. Write an account of the heating effect of electricity and show its application in lighting and in designing a fuse.

* These values have been modified by the author to correct a misprint in the original paper.

4. Describe the connection between combustion and human respiration.

5. What is meant by hardness in water? Give a simple explanation of the chemical methods of softening water.

6. How would you prepare chlorine in the laboratory? State its properties and applications.

PART II

CHAPTER XI

INTRODUCTION — ANALYSIS OF ORGANIC COMPOUNDS—TYPICAL ORGANIC COMPOUNDS

INTRODUCTION TO ORGANIC CHEMISTRY

Chemistry may be divided into two main branches, viz. Organic and Inorganic Chemistry. The subdivision was originally devised to differentiate between substances derived from living sources, and substances derived from inanimate sources. Thus substances from the latter sources were minerals, of earthy nature, resistant to fire, whilst materials composing living or animate matter were of an entirely different nature.

Early in the eighteenth century it was thought that different laws governed the two types of compound, and that the organic substances could only be produced through the agency of some vital force associated with the life of the plant or animal. Since then it has been shown that most organic compounds can be built up or synthesised in the laboratory, thus demonstrating that vital force is unnecessary in their constitution. With this discovery the original distinction between inorganic and organic compounds vanished, but another has been recognised.

The peculiar nature of the organic compounds is due to their construction. In them carbon is the fundamental element and it is usually found combined with oxygen and hydrogen: nitrogen, phosphorus, and sulphur being also often present. Thus, organic chemistry is the chemistry of carbon compounds.

On the other hand, in inorganic or mineral compounds there is no one particular element which is common to all of them as carbon is in organic compounds. Inorganic compounds are produced by union among all the metals and non-metals. Since there are many more metals than

non-metals, metallic compounds predominate in the inorganic world. The difference in nature between organic and inorganic compounds gives rise to important differences in their properties, which enable us to distinguish one from the other. Many organic compounds on heating, char,* due to the liberation of free carbon, e.g. starch behaves in this way. Thus a substance which chars on heating is probably organic, and if on further heating the charred mass burns completely away, the substance is undoubtedly organic in nature. If a small quantity of starch be heated on a crucible lid it will burn, leaving a charred mass. This burning represents the combustion of the hydrogen present and probably some of the carbon, part of the oxygen necessary coming from the air, and part already being present in the starch. If the heating be continued, the carbon burns completely away to carbon dioxide, leaving no solid residue:

$$\underset{\text{starch}}{C_6H_{10}O_5} \xrightarrow{\text{charring}} 6C + 5H_2O$$

$$6C + 6O_2 = 6CO_2$$

This, then, may be taken as a criterion of an organic compound, i.e. on heating it burns and chars, and on further heating burns completely away, leaving no solid residue.† If further proof of the organic nature of the substance be required, it may be obtained by heating it with copper oxide in a tube, and passing the products of combustion through lime water. The lime water will assume a milkiness due to precipitation of chalk by the carbon dioxide, and the water produced by the combustion of the hydrogen may be observed on the sides of the tube (Fig. 45). In this experiment the copper oxide supplies the oxygen necessary for the burning. With inorganic compounds, a solid residue is usually left behind on heating, though some substances could be mentioned which are completely volatile on heating. These, however, can readily be distinguished from organic compounds, by not charring and yielding products other than carbon dioxide on combustion. Substances of characteristic mineral nature, e.g. limestone, iron oxide, sand, on heating may suffer

* Those which do not char are either those which contain sufficient oxygen *to burn completely* the carbon or those which vaporise unchanged.

† Metallic derivatives of organic compounds leave a residue.

change, but all leave a solid residue due to their non-volatile nature. Inorganic substances, e.g. the ammonium salts which are completely volatile on heating, are readily distinguished from organic substances by the absence of charring and non-evolution of carbon dioxide.

Organic compounds are far more numerous than inorganic compounds. This may be ascribed in part to the unique properties possessed by the element carbon. Carbon has a valency of four, i.e. one atom of carbon may unite with four atoms of a monovalent element, which may be the same or all different ; or two atoms of a divalent element as in CO_2,

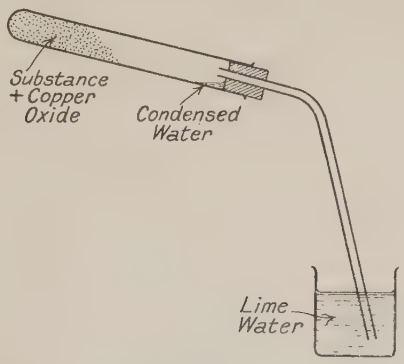


FIG. 45

CS_2. (These strictly are organic compounds, but for convenience are usually considered under inorganic compounds.) Thus, a great variety of derivatives may be obtained from quite a simple compound. Carbon has the remarkable property of uniting with itself, i.e. two, three or even much greater numbers of carbon atoms may link together, thus giving rise to the possibility of endless numbers of compounds.

In an examination of a compound, it is a simple matter to decide whether it contains the elements carbon and hydrogen. Oxygen is never tested for, its presence or otherwise being usually inferred from a complete quantitative analysis of the compound. When a new compound is discovered its analysis can be divided into two parts : *Qualitative Analysis*, in which the substance is examined to see *which* elements are present ;

Quantitative Analysis, in which the substance is examined to determine in what *proportions* the various elements are present. From this knowledge a formula for the body can be deduced.

The qualitative examination of a substance for carbon and hydrogen is conducted in the manner already described. The following elements which may be present in an organic compound, remain to be considered: halogen, i.e. chlorine, bromine; or iodine, nitrogen, sulphur, phosphorus.

Halogen. The substance is heated with a few small pieces of metallic sodium when the substance decomposes, and any halogen present forms the sodium compound, e.g. either NaCl, NaBr, or NaI. This is extracted from the residual mass with water, filtered, acidified with dilute nitric acid, and tested with silver nitrate solution. This yields a precipitate of either AgCl (white), AgBr (yellowish white), AgI (yellowish) if any halogen be present in the original body.

$$2Na + Cl_2 = 2NaCl$$

$$NaCl + AgNO_3 = AgCl + NaNO_3$$

$\downarrow$

insoluble white precipitate

Similar equations hold good for the other halogens. If nitrogen be present in the original substance sodium cyanide NaCN will be produced by the sodium fusion. This must be expelled as HCN by boiling with dilute nitric acid before testing with silver nitrate, since cyanides also give a white precipitate with $AgNO_3$.

Nitrogen. Many naturally occurring nitrogeneous compounds on heating alone, burn and give a characteristic smell described as that of "burnt hair." Such substances as hair, gelatine, feathers, horses' hoofs behave in this way. These same substances when heated with soda lime in a test tube give off part of their nitrogen in the form of ammonia (NH_3). This can be detected by its effect on a piece of moist red litmus paper. Dried gluten from wheat yields ammonia under these conditions. The most conclusive qualitative test for nitrogen is, however, the sodium fusion test. The substance is heated with sodium in a test tube. The carbon and nitrogen of the organic body unite with the sodium to form

sodium cyanide, NaCN. This is extracted with water, the solution filtered and treated as follows : A few drops of ferrous sulphate solution are added to the liquid which is then heated to boiling. The solution is then acidified with dilute hydrochloric acid and ferric chloride is added, when either a precipitate or intense blue colour due to the formation of Prussian blue is produced.

In the original filtered solution is always present some sodium hydroxide from the decomposition of water by the excess sodium used in the reaction :

$$2Na + 2H_2O = H_2 + 2NaOH$$

This reacts with the ferrous sulphate forming insoluble ferrous hydroxide :

$$2NaOH + FeSO_4 = Fe(OH)_2 + Na_2SO_4$$

On boiling, a reaction between ferrous hydroxide and any sodium cyanide in the solution occurs with the production of sodium ferrocyanide :

$$6NaCN + Fe(OH)_2 = \underset{\text{ferrocyanide}}{Na_4Fe(CN)_6} + 2NaOH$$

The production of Prussian blue by interaction of the sodium ferrocyanide and ferric chloride is indicative of the presence of nitrogen in the original organic compound :

$$3Na_4Fe(CN)_6 + 4FeCl_3 = \underset{\substack{\text{ferric ferrocyanide}\\ \text{Prussian blue}}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$

Sulphur. The substance is treated as for the halogen test, but to the filtered extract a solution of sodium nitroprusside is added, when an intense purple coloration is produced if any sulphur be present in the original compound. The sulphur in the organic body and the sodium unite to form sodium sulphide (Na_2S), which is soluble in water and forms the characteristic coloration with sodium nitroprusside.

Phosphorus. The substance is heated very cautiously in *small quantity*, with sodium peroxide * (Na_2O_2). The phosphorus in the organic body becomes oxidised to a phosphate, which may be tested for (after acidification with dilute nitric acid) by means of ammonium molybdate solution. This yields a characteristic yellow precipitate of ammonium phospho-molybdate.

* *Caution.*—Sodium peroxide reacts violently with any carbonaceous matter.

The quantitative analysis of a substance enables the percentage of each element present to be stated, and from this percentage composition may be deduced a formula for the compound. The quantitative estimation of carbon, hydrogen and nitrogen will be considered briefly. Carbon and hydrogen are usually determined together by Liebig's method. In principle, this consists in burning a known weight of substance and absorbing and weighing the carbon dioxide and water produced. From a knowledge of the composition of these two compounds, the amounts of carbon and hydrogen present in the substance can be calculated. Thus 1 molecule of CO_2 (44 parts) is produced from 1 atom of carbon (12 parts), i.e. $\frac{12}{44}$ of the weight of carbon dioxide formed is carbon. Similarly 1 molecule of H_2O (18 parts) is produced from 1 molecule of hydrogen (2 parts), i.e. $\frac{2}{18}$ or $\frac{1}{9}$ of the weight of water formed is hydrogen.

If the sum of the weights of carbon and hydrogen found is equal to the weight of substance taken for analysis, then no other element besides these two can be present in the compound. If nitrogen has been found qualitatively, then the quantity of nitrogen must be ascertained before it is possible to decide if or how much oxygen is present. Nitrogen may be determined in either of two ways :

(1) By burning a known weight of substance in a current of carbon dioxide. The nitrogen is collected and measured over a strong solution of caustic potash which absorbs all the CO_2. From the volume of nitrogen collected can be calculated the weight and hence the percentage of nitrogen in the original substance.

(2) The method commonly employed for the determination of nitrogen in foodstuffs is of special importance to milling students. Nitrogen is one of the fundamental constituents of proteins, a class of bodies essential to the growth of animals. The value of a foodstuff depends, among other things, on its protein content, and since the nitrogen content of most proteins is fairly constant, a nitrogen determination constitutes a most convenient method of arriving at the protein content of a foodstuff. The method commonly employed is termed the *Kjeldahl* method. In principle it consists in heating a known weight of substance with concentrated sulphuric acid, until the charred mass is converted to a colourless liquid.

During this heating, the carbon is oxidised to CO_2 by the hot concentrated acid, and the nitrogen is converted to ammonia, which remains in the flask as ammonium sulphate :

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$$

The liquid is cooled, diluted with water, transferred to the flask of a distillation apparatus made alkaline with caustic soda and the liberated ammonia is distilled into a known quantity of standardised hydrochloric acid solution :

$$(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O + 2NH_3$$

The hydrochloric acid remaining after the absorption of the ammonia is determined by titration with standard alkali. By difference the amount of hydrochloric acid neutralised by the ammonia may be found. From the equation

$$\underset{14+3}{NH_3} + \underset{1+35{\cdot}5}{HCl} = NH_4Cl$$

$$\underset{36{\cdot}5}{\underline{\quad\quad}}$$

it may be seen that

36·5 parts of HCl are neutralised by 17 parts NH_3,

corresponding to 14 parts N_2, e.g. in an experiment in which ·5096 gm. of substance were used, the ammonia was distilled over into a solution containing ·363 gm. HCl. After the absorption it was found that ·155 gm. HCl remained, i.e. ·363 − ·155 = ·208 gm. HCl were neutralised by the ammonia. Thus if

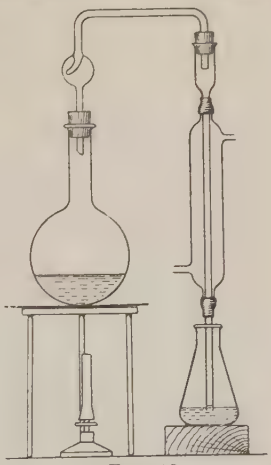


FIG. 46

36·5 gm. HCl are neutralised by 17 gm. NH_3 corresponding to 14 gm. N_2

$\therefore$ ·208 „ „ „ $\frac{17}{36{\cdot}5} \times {\cdot}208$ „ $\frac{14}{36{\cdot}5} \times {\cdot}208$ N_2

$= {\cdot}07975$ gm. N_2

i.e. ·5096 gm. substance contains ·07975 gm. N_2

100 gm. „ „ $\frac{{\cdot}07975}{{\cdot}5096} \times 100$

$= 15{\cdot}65$ per cent nitrogen

CLASSIFICATION OF ORGANIC COMPOUNDS

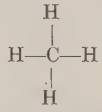
Owing to the enormous number of organic compounds which are known, it is necessary to classify them into more or less well defined groups in order that their relationships may be clearly understood.

The Hydrocarbons. The simplest group of organic compounds are those containing two elements only, viz. carbon and hydrogen. These are termed *hydrocarbons*. Several series of these are known ; e.g. :

(*a*) *The Paraffin series*, with a general formula C_nH_{2n+2}, where n may be 1, 2, 3, or 4, etc. Thus CH_4, methane ($n = 1$), is a gas found in ordinary coal gas ; C_2H_6, ethane ($n = 2$), a gas with similar properties to methane.

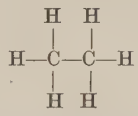
Since these bodies are constituted alike they have very similar properties, e.g. they are all combustible but otherwise relatively inert substances. The lower members (i.e. those containing the lesser number of carbon atoms) are gaseous, whilst the C_6 and C_7 members constitute ordinary petrol, and the higher members (C_{14}, etc.) are solids, e.g. paraffin wax, vaseline.

(*b*) *The Ethylene, Olefine or Unsaturated Series* have a general formula C_nH_{2n} (where n may be 2, 3, 4, etc.). The simplest members are C_2H_4 (n = 2), ethylene. and C_3H_6 ($n = 3$), propylene. These are gaseous combustible substances, but due to the fact that they do not contain a full complement of hydrogen per atom of carbon, they are said to be *unsaturated* and readily combine with other elements, e.g. hydrogen or bromine. One atom of carbon with valency of four is capable of uniting with four atoms of hydrogen or with other atoms equivalent to these. In methane this is realised : *

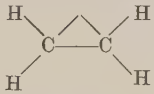


* It must be clearly understood that the strokes attached to the C atom have no *chemical* significance and represent merely a convenient, pictorial method of representing the ability of the C atom to combine with four atoms of hydrogen.

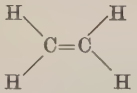
In ethane one valency of each of the carbon atoms is employed in uniting the two carbon atoms, thus :



whereas in ethylene, C_2H_4, only three of the valencies of each carbon atom are employed, the remaining one lying idle, thus :



Usually the two idle valencies are represented as saturating each other, thus :



Ethylene readily adds on hydrogen or bromine to form a saturated compound of the methane type.

(*c*) *The Acetylene Series* has the general formula C_nH_{2n-2}, of which the commonest and simplest member is acetylene, C_2H_2, or $H - C \equiv C - H$.

It will be seen that this is even more unsaturated than ethylene. Acetylene is combustible and is employed for illuminating purposes.

The Alcohols. Related to the hydrocarbons are the *alcohols*. These may be conveniently regarded as substitution products of the hydrocarbons. In organic compounds it is often possible to replace the atoms of certain elements by those of others. The resulting products are termed *substitution products*. It is not always actually possible to carry out this substitution easily or in one step. Thus alcohols can be regarded as hydroxy substitution derivatives of the hydrocarbons, but the alcohols concerned are not necessarily prepared by substitution in hydrocarbons, since simpler methods are available for their production. Hydroxy substitution products of hydrocarbons are bodies in which one or more of the hydrogen atoms of the hydrocarbon are replaced by hydroxyl or (OH) groups. Thus methyl alcohol (CH_3OH)

may be regarded as methane $CH_3.H$ with one hydrogen atom replaced by an OH group. Likewise $C_2H_5.OH$, ethyl alcohol, is derived from ethane $C_2H_5.H$ by the replacement of one hydrogen atom by an hydroxyl group. The group of atoms united with the hydroxyl group, e.g. CH_3, or C_2H_5, is termed a *radical*, and behaves as if it were a single atom; the OH group may also be termed a radical. Thus the simple alcohols mentioned above can be compared with inorganic hydroxides. In fact, they have some properties very similar to those of the inorganic hydroxides. Compare the two reactions :

$NaOH$ sodium hydroxide	+	HCl hydrogen chloride	=	$NaCl$ sodium chloride	+	H_2O water
CH_3OH methyl hydroxide or methyl alcohol	+	HCl hydrogen chloride	=	CH_3Cl methyl chloride	+	H_2O water

The first reaction represented the neutralisation of an acid by an alkali to form a salt and water; in the second the alcohol is behaving like an hydroxide, yielding methyl chloride (a kind of salt termed an *ester*) and water.

It might be mentioned in passing that the second reaction does not take place to completion unless some agent, $ZnCl_2$, zinc chloride, be present to remove the water as fast as it is formed. Otherwise the reactions are remarkably alike.

Of the many alcohols known, perhaps those derived from the methane series are the most important. These simple alcohols containing one OH group are termed *monohydric alcohols*, and may be represented by the general formula R.OH, where R = any organic radical of the methane series, or by $C_{n_2n}H_{+1}.OH$, for methyl alcohol $n = 1$ and for ethyl alcohol $n = 2$. Alcohols in other series are known, containing two and sometimes three OH groups, e.g. ethylene glycol $\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}$ may be regarded as ethane $\begin{matrix}CH_3\\|\\CH_3\end{matrix}$ with two hydrogen atoms replaced by OH groups, and $\begin{matrix}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{matrix}$ glycerol

(or glycerine) may be regarded as propane $\begin{matrix}CH_3\\|\\CH_2\\|\\CH_3\end{matrix}$ with three hydrogen atoms replaced by OH groups. These alcohols are termed *dihydric* and *trihydric* alcohols respectively. Alcohols as a class may be characterised by the OH group which they contain. They have the following general properties :

(1) They form " esters " on suitable treatment with an acid. The esters formed with organic acids are many in number and their constitution has something in common with that of inorganic salts, e.g. :

$$\underset{\text{ethyl alcohol}}{C_2H_5OH} + \underset{\text{acetic acid}}{CH_3COOH} = \underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

$$NaOH + CH_3COOH = \underset{\text{sodium acetate}}{CH_3COONa} + H_2O$$

(2) The alcohols of the methyl alcohol series on oxidation with potassium dichromate ($K_2Cr_2O_7$) and sulphuric acid, lose two atoms of hydrogen forming *aldehydes*, e.g. :

$$CH_3OH + \underset{\text{from oxidising agent}}{O} = \underset{\text{formaldehyde}}{CH_2O} + H_2O$$

(3) The hydrogen of the OH group is replaceable by treatment with metallic sodium to form metallic derivatives ; e.g. :

$$2R{\cdot}OH + 2Na = 2R{\cdot}ONa + H_2$$

Cf.

$$2{\cdot}H{\cdot}OH + 2Na = \underset{\text{sodium hydroxide}}{2H{\cdot}ONa} + H_2$$

Methyl alcohol or methanol,* CH_3OH, is produced during the destructive distillation of wood ; hence the name " wood spirit." It is a liquid, boiling point 65° C., lighter than water, and mixes with water in all proportions.

Ethyl alcohol or ethanol, C_2H_5OH. This is present in wine and beer and all fermented liquors. Often referred to as " spirits of wine." It is produced commercially by the fermentation of sugary liquids. (See section on Fermentation.) As produced by fermentation the alcohol is present only as a dilute solution in water. By distillation, stronger spirit may be obtained (about 80 per cent), but to obtain 100 per cent ethyl alcohol (absolute alcohol) the water must be removed by some drying agent, e.g. CaO, quicklime.

* Alcohols are sometimes systematically named by adding the termination *ol* to the name of the hydrocarbon from which they are derived.

Pure ethyl alcohol is a liquid, boiling point 78°, and is lighter than water. It mixes with water in all proportions, accompanied by a contraction in volume. The strength of an alcoholic liquid may be determined from its density. Density of water = 0·99905 at 15·5° C. Density of ethyl alcohol = ·7935 at 15·5°. All possible mixtures of alcohol and water must have densities lying between these two values. Tables giving the density and the corresponding composition of the alcohol-water mixture are to be found in chemical treatises. The commonest strengths of spirit are :

(1) Rectified spirits of wine, 84 per cent absolute alcohol by weight.
(2) Proof spirit, having density $\frac{12}{13}$ at 10° C. This contains 49·24 per cent alcohol by weight.
(3) Absolute alcohol, being 100 per cent C_2H_5OH.

Methylated spirit consists of ethyl alcohol, to which has been added some substance with a sufficiently nauseating flavour to render the liquor unfit for drinking purposes. Crude wood spirit or light paraffins are used for this purpose. Methylated spirit contains approximately 90 per cent by volume of rectified spirits of wine, and can be used for most ordinary laboratory operations instead of rectified spirits. Being deemed unfit for drinking purposes no excise duty is paid on methylated spirits.

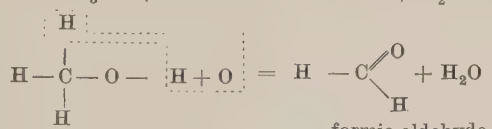
Glycerine or *Glycerol*, $C_3H_5(OH)_3$. This is a trihydric alcohol, i.e. contains three OH groups. It yields three esters according to the number of OH groups which react with the acid, e.g. :

$CH_2O{\cdot}OC{\cdot}CH_3$	$CH_2O{\cdot}OC{\cdot}CH_3$	$CH_2O{\cdot}OC{\cdot}CH_3$
|	|	|
$CHOH$	$CHO{\cdot}OC{\cdot}CH_3$	$CHO{\cdot}OC{\cdot}CH_3$
|	|	|
CH_2OH	CH_2OH	$CH_2O{\cdot}OC{\cdot}CH_3$
mono acetin or glycerol mono-acetate	diacetin or glycerol diacetate	triacetin or glycerol triacetate

The corresponding esters of some of the higher fatty acids, e.g. palmitic acid and stearic acid, are found as constituents of natural oils and fats. Glycerol is a thick syrupy liquid with a sweet taste, and is produced by the hydrolysis of natural fats. It is formed also in small quantities during the normal fermentation of sugar.

The Aldehydes. These may be regarded as derived from the simple alcohols, like methyl and ethyl alcohol, by the removal of two atoms of hydrogen. This removal is accomplished during the course of an oxidation operation, when the two hydrogen atoms unite with one atom of oxygen. Hence the name aldehyde from "*al*cohol *dehyd*rogenatum." The oxidation may be carried out by means of potassium dichromate ($K_2Cr_2O_7$) and concentrated sulphuric acid :

$$CH_3OH + O = H{\cdot}CHO + H_2O$$



formic aldehyde
or
formaldehyde

Similarly :

acetic aldehyde, or
acetaldehyde

The aldehydes are named from the acids which they yield on further oxidation, and not from the alcohols from which they are formed. The characteristic grouping of aldehydes is the —CHO grouping, which confers certain general properties on all bodies containing that group.

General Characteristic Properties of bodies containing —CHO *grouping.*

(1) By further oxidation an atom of oxygen is added on, forming the —COOHgroup, characteristic of all organic acids :

$$R{\cdot}CHO + O = R{\cdot}COOH$$

or

$$\underset{\text{acetaldehyde}}{CH_3{\cdot}CHO} + O = \underset{\text{acetic acid}}{CH_3{\cdot}COOH}$$

(2)By reason of the ease with which these aldehydes combine with oxygen, they act as reducing agents,* e.g. they reduce ammoniacal silver oxide or Fehling's solution, the former to metallic silver, the latter to the lower oxide of copper (Cu_2O).

* A reducing agent is one which readily removes oxygen from or adds hydrogen on to another body.

In the former case, if diluted ammonia be added to diluted silver nitrate solution, a precipitate of silver oxide is produced, which immediately dissolves in excess of ammonia :

$$2AgNO_3 + 2NH_4OH = Ag_2O + 2NH_4NO_3 + H_2O.$$

If this solution is carefully warmed with a body containing an aldehyde group, the silver oxide is reduced to silver, which is deposited in the sides of the tube as a shiny mirror, e.g. :

$$Ag_2O + H{\cdot}CHO = 2Ag + \underset{\text{formic acid}}{H{\cdot}COOH}$$

Many of the sugars, which contain an aldehyde grouping, give a positive reaction with this test.

Fehling's Solution. If a solution of sodium hydroxide be added to a solution of copper sulphate, a light blue precipitate of copper hydroxide is thrown down :

$$2NaOH + CuSO_4 = \underset{\text{copper hydroxide}}{Cu(OH)_2} + Na_2SO_4$$

If the solution be now boiled, the hydroxide loses a molecule of water and black copper oxide remains :

$$\underset{\text{hydroxide}}{Cu(OH)_2} = \underset{\text{oxide}}{CuO} + H_2O$$

If, before the addition of the sodium hydroxide, the copper sulphate be mixed with a solution of sodium potassium tartrate (Rochelle Salt), then no precipitation occurs, but a deep blue solution results. [Tartrates prevent the precipitation of metals as hydroxides by sodium hydroxide.] This deep blue solution can be regarded as a source of copper oxide (CuO black), for when heated with a reducing agent like an aldehyde the following reaction occurs :

$$\begin{array}{l} Cu{:}O + H{\cdot}CHO \\ + \\ \underset{\text{black}}{CuO} \end{array} = \begin{array}{l} Cu \\ \diagdown \\ O + H{\cdot}COOH \\ \diagup \\ \underset{\text{red}}{Cu} \end{array}$$

The red copper oxide does not remain in solution with the tartrate but is thrown down as a bright red precipitate. If required, the red precipitate may be filtered off, dried, and weighed, and since a proportionality exists between the red oxide and the aldehyde necessary to produce it, the weight of the oxide obtained serves as an index of the amount of aldehyde originally present.

Since the deep blue solution, known as Fehling's solution, does not keep well, the copper sulphate solution and alkaline tartrate solutions are mixed in equal volume immediately before use.

(3) By suitable reducing agents, aldehydes can be reduced to the corresponding alcohols :

$$\underset{\text{hydrogen}}{\overset{\text{atomic}}{\longrightarrow}}$$

$$H{\cdot}CHO \longrightarrow H{\cdot}CH_2OH$$

methyl alcohol

(4) By reason of the doubly linked oxygen atom in the aldehyde group, $-C\begin{matrix}O\\ \diagup\!\!\diagdown\\ H\end{matrix}$, many additive compounds are formed by aldehydes.

Formaldehyde, H.CHO. This may be formed by the oxidation of methyl alcohol, using a catalyst. The vapour of methyl alcohol with air is passed through a hot tube containing platinum gauze as a catalyst. Formaldehyde is a gas, soluble in water and with a peculiar acrid smell. Its aqueous solution is sold as a commercial product, under the title " Formalin," and is used as a disinfectant ; formerly it was added to foodstuffs as a preservative. It has been shown recently that formaldehyde is produced during the process of photosynthesis in plants, i.e. the process of building up complex organic substances, like sugar and starch, from carbon dioxide and water in the presence of sunlight and chlorophyll. (See Appendix, p. 127.)

The probable mechanism is as follows :

Carbon dioxide and water in the presence of sunlight and " chlorophyll " (the green colouring matter in all plants), react to form formaldehyde and oxygen is liberated :

$$CO_2 + H_2O = H{\cdot}CHO + O_2$$

This change has actually been accomplished in the laboratory. In the plant, the formaldehyde then undergoes a process of condensation with itself, to varying extents, to produce complex substances like sugar and starch, e.g. :

$$6H{\cdot}CHO = \underset{\text{glucose}}{C_6H_{12}O_6}$$

$$2C_6H_{12}O_6 = \underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2O$$

$$n(C_6H_{12}O_6) = \underset{\text{starch}}{(C_6H_{10}O_5)n} + nH_2O$$

Acetaldehyde is a low boiling point liquid, which may be prepared by the oxidation of ethyl alcohol with potassium dichromate and sulphuric acid :

$$\underset{\text{ethyl alcohol}}{CH_3{\cdot}CH_2OH} + \underset{\text{from oxidiser}}{O} = \underset{\text{acetaldehyde}}{CH_3{\cdot}CHO} + H_2O$$

Organic Acids may be characterised by the presence of the —COOH or carboxyl group. They are related to the aldehydes, being formed from these by oxidation :

$$H{\cdot}CHO + O = \underset{\text{formic acid}}{H{\cdot}COOH}$$

Those containing one —COOH group are termed monocarboxylic acids, e.g. H.COOH, whilst those containing two carboxylic groups are referred to as dicarboxylic acids, e.g. :

$\begin{matrix}COOH\\|\\COOH\end{matrix}$, oxalic acid.

The series of acids theoretically derivable from the methane hydrocarbons, via the corresponding alcohol and aldehyde, are termed the *fatty acids*, since the higher members are to be found in natural fats, e.g. stearic and palmitic acids. The general formula of this series is $C_nH_{2n+1}{\cdot}COOH$. The first few members of the series are :

$H{\cdot}COOH$, Formic acid ($n = 0$)
$CH_3{\cdot}COOH$, Acetic acid ($n = 1$)
$CH_3{\cdot}CH_2{\cdot}COOH$, Propionic acid ($n = 2$)
$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, Butyric acid ($n = 3$)

The general properties of these acids are as follows :

(1) The acid property is inherent in the COOH group, the H atom of which is replaceable by metals forming salts. (See definition of acid, Part I, p. 36.)

(2) The general properties of acids as illustrated by inorganic acids are also possessed by these organic acids ; the stronger acids react alkaline to litmus. Most of them effer-

vesce with Na_2CO_3, expelling the carbon dioxide; they neutralise bases and alkalies, forming salts and water, thus:

$$H{\cdot}COOH + NaOH = \underset{\text{sodium formate}}{H{\cdot}COONa} + H_2O$$

(3) On suitable reduction they yield first an aldehyde and then the corresponding alcohol.

Formic acid, H.COOH or H_2CO_2. This is a liquid which may be obtained by distilling red ants. It is readily soluble in water. On treatment with concentrated sulphuric acid, formic acid (or formates) yield carbon monoxide:

$$H{\cdot}COOH \quad - \quad \underset{\text{withdrawn by } H_2SO_4}{H_2O} \quad = \quad CO.$$

For this reason carbon monoxide is sometimes regarded as the anhydride of formic acid, just as carbon dioxide is the anhydride of carbonic acid (H_2CO_3), and sulphur trioxide of sulphuric acid (H_2SO_4). Under some circumstances carbon monoxide will unite directly with potassium hydroxide to yield potassium formate:

$$KOH + CO = \underset{\text{potassium formate}}{H{\cdot}COOK}$$

Acetic Acid, CH_3COOH. This may be made in the laboratory by the oxidation of acetaldehyde or of ethyl alcohol by means of potassium dichromate and sulphuric acid. It is produced commercially, however, in the manufacture of vinegar, by the oxidation of ethyl alcohol by oxygen of the air through the agency of a micro-organism.

In the manufacture of vinegar, weak wine or beer is allowed to trickle slowly over beech-wood shavings in a special ventilated barrel. The beech-wood shavings have previously been impregnated with a micro-organism, *mycoderma aceti*. This micro-organism is one which requires a plentiful supply of air in order to grow and multiply. As a result of the life process of the organism, a body termed an *enzyme* is elaborated which enables the oxygen of the air to oxidise the alcohol, first to aldehyde and finally to acid:

$$2C_2H_5OH + O_2 = 2CH_3CHO + 2H_2O$$
$$2CH_3CHO + O_2 = 2CH_3COOH.$$

This change is a type of fermentation (acetic fermentation), which is a general term applied to the chemical changes which

occur during the life process and development of certain micro-organisms.

Acetic acid is produced commercially to-day by either of two methods : (*a*) by the destructive distillation of wood, or (*b*) by synthetic methods starting from calcium carbide (CaC_2). This is treated with water to yield acetylene gas which is hydrated catalytically to give acetaldehyde :

$$C_2H_2 + H_2O = CH_3{\cdot}CHO$$

The acetaldehyde is oxidised by oxygen of the air to yield acetic acid. Acetic acid is a low melting point solid (melting point 17° C.) with a sharp smell, easily soluble in water, and gives rise to salts, viz. acetates.

Propionic acid ($CH_3.CH_2COOH$) is of little importance to a flour milling student, and a description of this acid will be omitted.

Butyric acid, $CH_3.CH_2.CH_2.COOH$ or $C_3H_7.COOH$, is a liquid with a particularly disagreeable smell. It is present in rancid butter, sweat, etc. It may be found among the products of putrefaction of many organic substances. Putrefaction may be classed as a kind of fermentation, since it is brought about by micro-organisms ; it may be referred to as "putrefactive fermentation." When cheese putrefies, a micro-organism, *the butyric ferment*, develops and multiplies in it. If this cheese be used as a source of the micro-organism and is added to sour milk, a chemical change occurs, referred to as *butyric fermentation*, resulting in the production of butyric acid.

Milk exposed to air turns sour through the agency of yet another micro-organism (the lactic ferment), which converts the sugar of milk (lactose) to lactic acid. This is then converted by the butyric ferment to butyric acid. The chemical changes occurring may be represented as follows :

$$\underset{\text{lactose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{ferment}]{\text{lactic}} \underset{\text{lactic acid}}{4C_3H_6O_3}$$

$$4C_3H_6O_3 \xrightarrow[\text{ferment}]{\text{butyric}} \underset{\text{butyric acid}}{2C_4H_8O_2} + 4CO_2 + 4H_2$$

The Higher Fatty Acids. Palmitic acid and stearic acid occur combined with glycerol as the glyceryl esters in many natural fats. During the manufacture of common soap, the fats are

hydrolysed by boiling with sodium hydroxide solution, forming the sodium salts of the fatty acids and free glycerol. The glycerol is distilled off with steam at reduced pressure, and the sodium salts left in the solution constitute common hard soap. Both glyceryl palmitate and stearate are commonly present in the fats used, so that the soaps obtained are mixtures of sodium salts of these fatty acids :

$$\begin{array}{l} CH_2O{\cdot}OC{\cdot}C_{15}H_{31} \\ | \\ CHO{\cdot}OC{\cdot}C_{15}H_{31} \\ | \\ CH_2O{\cdot}OC{\cdot}C_{15}H_{31} \\ \text{glyceryl palmitate} \end{array} + \begin{array}{l} NaOH \\ \\ NaOH \\ \\ NaOH \end{array} = \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{glycerol} \end{array} + \begin{array}{l} C_{15}H_{31}{\cdot}COONa \\ \\ C_{15}H_{31}{\cdot}COONa \\ \\ C_{15}H_{31}{\cdot}COONa \\ \text{sodium palmitate} \end{array}$$

The equation is similar for glyceryl stearate if $C_{17}H_{35}.COOH$, the formula for stearic acid, be substituted for that of palmitic acid.

Lactic acid.$C_3H_6O_3$ or $CH_3.CH(OH).COOH$. This acid is a derivative of one of the fatty acids ; namely, it is hydroxy-propionic acid, i.e. an OH group replaces one of the H atoms of the CH_2 group of propionic acid. Lactic acid is present in sour milk, where it is produced from the lactose by the *lactic ferment*, which finds its way into the milk from the atmosphere. It is a low melting solid (melting point 18° C.) with a sour smell and taste. It is soluble in water and forms salts called lactates.

Succinic acid, $\begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}$. A di-carboxylic acid belonging to the oxalic acid series. The general formula for this series is $(CH_2)_n.(COOH)_2$.

For oxalic acid, $n = 0$ ..... $\begin{array}{l} COOH \\ | \\ COOH \end{array}$

malonic acid, $n = 1$ ..... $\begin{array}{l} COOH \\ \diagup \\ CH_2 \\ \diagdown \\ COOH \end{array}$

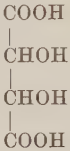
succinic acid, $n = 2$ ..... $\begin{array}{l} CH_2{\cdot}COOH \\ | \\ CH_2{\cdot}COOH \end{array}$

Succinic acid is a solid, easily soluble in water, and forms salts —succinates. Being a dicarboxylic acid, it forms, of course, two sodium salts. Succinic acid is produced in *traces* during

normal alcoholic fermentation, i.e. it is produced in traces during fermentation during bread-making processes.

It has been shown that acidity has an important effect on the condition of the dough during bread-making. It has the effect of bringing the dough to such a physical state as to be most beneficial to the production of a good loaf. It is probable that succinic acid contributes towards this increased acidity on fermentation.

Tartaric acid.

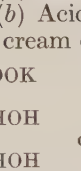


, dihydroxy succinic acid. This substance occurs in grape juice, and during fermentation it is deposited as an insoluble solid termed *argol*. This body is a crude potassium hydrogen tartrate.

Tartaric acid is a dibasic acid (i.e. contains two carboxyl groups, each with a replaceable hydrogen atom), and forms two potassium salts :

(*a*) Normal or neutral potassium tratrate.

(*b*) Acid potassium tartrate or potassium hydrogen tartrate, or cream of tartar.



or $K_2(C_4H_4O_6)$

normal potassium tartrate

or $KH(C_4H_4O_6)$.

cream of tartar

Cream of Tartar has an acid reaction, since it still contains one hydrogen atom replaceable by metals, e.g. like any other acid it will liberate CO_2 from sodium bicarbonate or sodium carbonate.

Baking powder mixtures often contain sodium bicarbonate mixed in a perfectly dry state with potassium hydrogen tartrate, together with some agent to keep the materials dry, usually rice starch. On the addition of water, especially at elevated temperatures, the components of the mixture dissolve and interact, liberating CO_2 and leaving behind a residue of sodium potassium tartrate, $NaK(C_4H_4O_6)$, Rochelle Salt :

$$\begin{array}{l} \text{COOK} \\ | \\ \text{CHOH} \\ | \\ \text{CHOH} \\ | \\ \text{COOH} \end{array} + NaHCO_3 = \begin{array}{l} \text{COOK} \\ | \\ \text{CHOH} \\ | \\ \text{CHOH} \\ | \\ \text{COONa} \end{array} + CO_2 + H_2O$$

Rochelle salt

Esters are bodies formed by the interaction of an alcohol with an acid, generally an organic acid. Water is the other product. The inorganic analogues are the *salts*. Most esters are hydrolysed more or less rapidly by water, reforming the original alcohol and acid. The presence of alkali facilitates this reaction. Hence, in ester formation, some agent must be present to remove the water as fast as it is formed (usually H_2SO_4 or $ZnCl_2$), e.g. the formation of ethyl acetate can be represented :

$$CH_3COOH + C_2H_5OH \underset{\text{hydrolysis in presence alkali}}{\overset{\text{esterification in presence } H_2SO_4}{\rightleftharpoons}} CH_3COOC_2H_5 + H_2O$$

Esters are usually sweet-smelling substances, many of them being employed for flavouring purposes, e.g. amyl acetate has a pear, and ethyl butyrate has a pineapple flavour. Many natural fats are esters. The alcohol is usually glycerol, whilst the acids commonly found are stearic, palmitic, and oleic acids. The oil which may be extracted by ether from the germ of wheat is of a light yellow colour, consisting largely of glyceryl oleate with some glyceryl palmitate, and stearate. On keeping, this oil tends to become rancid, or acid, probably due to slow oxidation. Thus the presence of the germ in flour would render the flour liable to become rancid. The difficulty may be overcome by either removing the germ altogether or replacing it in the flour after it has been cooked. The cooked germ does not tend to become rancid.

Considering now the more important classes of complex organic compounds, the following are of interest to the student of flour milling :

Carbohydrates. These must not be confused with hydro-

carbons which contain only the elements hydrogen and carbon. The carbohydrates contain the elements carbon, hydrogen, and oxygen, the latter two elements being present always in the same proportions as they are present in water, viz. two atoms hydrogen to one atom of oxygen. Carbohydrates may be subdivided into three groups according to their complexity. Those containing less than six atoms of carbon will not be considered.

Hexoses or *Monosaccharides*, of general formula $C_6H_{12}O_6$. Of these, several are known, the chief of which are : (*a*) glucose or dextrose, (*b*) fructose or lævulose, (*c*) galactose. The difference between these bodies will be considered later.

Dihexoses or *Disaccharides*, of general formula $C_{12}H_{22}O_{11}$. These can be considered as being derived from two molecules of a hexose, with the elimination of one molecule of water. Various combinations of the hexoses give rise to several disaccharides. Thus, maltose on hydrolysis yields two molecules of glucose, i.e. maltose can be regarded as two glucose molecules, condensed with the loss of a molecule of water :

$$\underset{\text{glucose}}{C_6H_{10}O_6} + \underset{\text{glucose}}{C_6H_{10}O_6} \underset{\text{hydrolysis}}{\rightleftharpoons} \underset{\text{maltose}}{C_{12}H_{22}O_{11}} + H_2O$$

Similarly, cane sugar yields on hydrolysis one molecule of glucose and one of fructose, and lactose one molecule galactose and one of fructose.

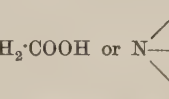
Polyhexoses or *Polysaccharides*, of general formula $(C_6H_{10}O_5)_n$ and sometimes also termed *amyloses*. These include starch, cellulose, and dextrin. These may be regarded as n (some unknown number) hexose molecules, condensed with the elimination of n molecules of water. Thus :

$$n(C_6H_{12}O_6) = nH_2O + (C_6H_{10}O_5)n$$

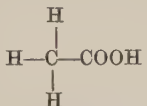
Ordinary starch is an exceedingly complex compound, the suffix n in the above formula being of the order of 200. Cellulose is at least as complex as starch, whilst in dextrin, a product of the hydrolysis of starch, n is of the order of 40. The carbohydrates will be dealt with in more detail in a subsequent chapter.

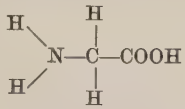
Proteins. This class of bodies is perhaps the most important in wheat and flour. Substances of this class are of an extremely complex nature, and are characterised by their

nitrogen content. It has been shown, in recent years, that proteins consist of a number of amino-acid residues linked together. These amino-acids may be regarded either as derivatives of ammonia (NH_3), or of a fatty acid. Thus the simplest amino-acid is amino-acetic acid (glycine):

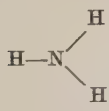
$NH_2 \cdot CH_2 \cdot COOH$ or 

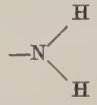
Glycine may also be regarded as acetic acid in which one hydrogen atom of the $-CH_3$ radical has been replaced by an amino group:

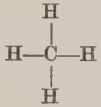

acetic acid

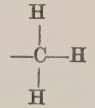

amino acetic acid

The NH_2 group or radical is a common one in nitrogeneous compounds and bears the same relation to ammonia as the methyl radical does to methane:


ammonia


amino radical ($-NH_2$)


methane


methyl radical ($-CH_3$)

An amino-acid contains both a basic group (NH_2) and an acid group (COOH), and under certain circumstances may behave as either a base or an acid. It has been shown that molecules of the same or different amino-acids readily link together to form complex bodies that resemble proteins. Likewise proteins, on hydrolysis, yield amino-acids. The linking up may be presumed to occur as follows:

$$NH_2 \cdot CH_2CO \cdot OH + H \cdot NH \cdot CH_2 \cdot CO \cdot OH + H \cdot NH \cdot CH_2COOH,$$

to give a complex substance:

$$NH_2 \cdot CH_2CO \cdot NH \cdot CH_2CO \cdot NH \cdot CH_2COOH$$

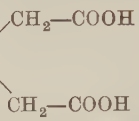
Where linkage between different amino-acids occurs it is obvious that extremely complicated bodies can be obtained.

Chief among the products of hydrolysis of the gliadin from

wheat is glutamic acid, amino-glutaric acid :

$$COOH.CH.(NH_2).CH_2.CH_2.COOH$$

Glutaric acid is a dicarboxylic acid next in series to succinic acid and has the formula :



Glutenin from wheat on hydrolysis only yields half the quantity of glutamic acid that is provided by gliadin, thus establishing the difference between the two proteins.

CHAPTER XII

CARBOHYDRATES—SUGARS—STARCH—CELLULOSE

THESE may be classified into :

(*a*) Hexoses or Monosaccharides, of formula $C_6H_{12}O_6$.
(*b*) Dihexoses or Disaccharides, of formula $C_{12}H_{22}O_{11}$.
(*c*) Polyhexoses or Polysaccharides, of formula $(C_6H_{10}O_5)_n$.

The Hexoses. Carbohydrates in general are polyhydroxy open chain compounds, usually either aldehydes or ketones (i.e. contain the $=CO$ group, e.g. $\begin{matrix}CH_3\\CH_3\end{matrix}>CO$ dimethyl ketone or acetone). Those which are aldehydic in nature are termed *aldoses*, and can be represented generally by glucose, $CH_2OH.(CHOH)_4.CHO$, and those which are ketonic are termed *ketoses*, and can be represented by lævulose, $CH_2OH.(CHOH)_3.CO.CH_2OH$.

The aldoses have the general properties of aldehydes, e.g. they may be reduced to the corresponding alcohol or oxidised to the corresponding acid.

A number of different aldoses and ketoses are known ; they differ in the arrangement of the OH and H groups, in the CHOH groups, and also in their behaviour towards plane polarised light.*

Glucose, sometimes termed dextrose or grape sugar, occurs

* See Appendix.

naturally in ripe fruits. It is a colourless, crystalline solid, easily soluble in water and less sweet than cane sugar. It is produced along with fructose by the hydrolysis of cane sugar.

Glucose is manufactured in large quantity by the hydrolysis of starch for use in the confectionery and brewing industry. The starch is heated with dilute sulphuric acid under pressure, the resulting liquor neutralised with chalk, clarified through bone charcoal and evaporated in vacuo. The commercial article varies from a colourless syrup to a dark brown solid.

Glucose is a typical aldose. It reduces ammoniacal silver oxide and Fehling's solution. It is also directly fermentable by yeast (difference from cane sugar). A solution of glucose rotates the plane of polarised light to the right, i.e. it is dextro-rotatory, hence its known " dextrose."

Fructose, also termed lævulose or fruit sugar, occurs along with glucose in ripe fruits. Fructose may be prepared by hydrolysing cane sugar with dilute sulphuric acid. After neutralisation, the addition of lime causes the precipitation of the insoluble calcium compound of fructose whilst that of glucose is soluble.

Fructose is a whitish yellow crystalline substance, easily soluble in water and much sweeter than glucose. It is a typical ketose, and as such reduces Fehling's solution and ammoniacal silver oxide less readily than glucose. Likewise it is less easily fermented by yeast than glucose. Fructose rotates the plane of polarised light to the left, i.e. it is lævo-rotatory ; hence its name lævulose.

When cane sugar is hydrolysed with dilute sulphuric acid, for every molecule of fructose produced, one molecule of glucose is formed. Thus the product is a mixture of fructose and glucose. This mixture is termed *invert sugar*, and the operation *the inversion of cane sugar*. Cane sugar is dextro-rotatory, and of the products, fructose is more lævo-rotatory than glucose is dextro-rotatory, hence the net result is a lævo-rotatory mixture, i.e. the direction of rotation has been inverted during the hydrolysis of the cane sugar :

$$\underset{\substack{\text{cane sugar}\\ \text{dextro}}}{C_{12}H_{22}O_{11}} \xrightarrow{+\ H_2O} \underbrace{\underset{\substack{\text{glucose}\\ \text{dextro}}}{C_6H_{12}O_6} + \underset{\substack{\text{fructose}\\ \text{strongly lævo}}}{C_6H_{12}O_6}}_{\text{lævo}}$$

Galactose does not occur free in nature, but is formed, with glucose, by the hydrolysis of lactose (the sugar of milk) with dilute sulphuric acid. It is a crystalline substance, soluble in water, but is only slightly sweet to the taste. It is an aldose in many respects similar to glucose.

The Dihexoses. *Cane Sugar*, also termed Saccharose or Sucrose. This occurs naturally in the sugar cane and sugar beet. The juices of the former contain 18 per cent whilst those of the latter from 14 to 18 per cent of sucrose. Sucrose is a well-crystallised solid, readily soluble in water. On heating, the sugar passes through a series of changes till finally, by loss of inflammable gases, a residue of sugar charcoal is left.

Sucrose does not reduce Fehling's solution, nor ammoniacal silver oxide, indicating that it contains neither aldehyde nor ketone grouping.

On boiling sucrose with dilute sulphuric acid, hydrolysis occurs with the formation of glucose and fructose. The resulting solution will then (after neutralisation) reduce Fehling's solution and ammoniacal silver oxide.

It should be noted too that yeast has no immediate effect on cane sugar. It is only after *inversion* to glucose and fructose that fermentation sets in. This inversion is brought about by a substance present in the yeast. A solution of sucrose is dextro-rotatory, and the amount of sucrose in a given solution may be determined by measurement of the rotation of the plane of polarised light brought about by the sugar solution.

Lactose or *milk sugar* is present in milk to the extent of about 4–5 per cent, and may be obtained by the evaporation of skimmed milk. It is a white crystalline solid, moderately soluble in water and faintly sweet to taste. It readily reduces Fehling's solution, but is not fermented by yeast. On hydrolysis, glucose and galactose result. It may also be readily converted into lactic acid through the agency of a micro-organism present in the air and termed the *lactic ferment*:

$$\underset{\text{lactose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{lactic acid}}{4C_3H_6O_3}$$

It is to this reaction, which occurs when milk is exposed to air, that the souring of milk is due.

Maltose or *Malt Sugar*. By the hydrolysis of starch with dilute acid, maltose is to be found among the first products along with another carbohydrate body termed *dextrin*. The chief final product of the hydrolysis is glucose. Maltose is commonly produced, however, by the action of an *enzyme* * on starch. This enzyme, termed *diastase*, has the specific property of converting starch to sugars. It is elaborated during the germination of cereals, and its usual source is germinated barley, produced during the process of malting. Barley, after dry cleaning, is steeped in water, drained, and placed in long shallow heaps. Germination commences (i.e. the corn commences to grow) and the temperature rises. The mass is turned over periodically to aerate it and prevent overheating. As germination proceeds, rootlets appear, and sundry enzymes develop. After a period of about nine days, the " green malt " is heated to check further growth, and dried off by slowly heating in a kiln. The green malt so obtained is used as a source of sundry commercial articles. It is milled to produce " malt flour." This is sometimes added by bakers to flour before bread-making to improve the loaf. Malt flour assists gas production by providing maltose, upon which the yeast acts to form carbon dioxide. It also contains the enzyme diastase, which converts starch to maltose, thus providing more sugar for the yeast. Malt flour, which contains usually about 8–9 per cent maltose, may thus be used to improve a flour deficient in gas production, i.e. normal sugar content. Malt flour not only contains maltose but also contains the enzyme diastase which is capable of producing maltose from starch.

Green malt is also extracted with hot water to yield " malt extract." The crushed grain is treated with water at a temperature of about 62° C. for some three hours. During this time the starch is converted by the diastase to maltose (and dextrin). After filtration, the liquor is evaporated in vacuo to a thick syrup, which is the commercial article termed " malt extract." It contains on an average about 60 per cent of maltose.

The following figures show the composition of an average sample of commercial malt extract :

* See page 177.

Water	22·23 per cent
Mineral matter	1·10 ,,
Proteins	3·01 ,,
Dextrin	12·90 ,,
Sucrose	3·59 ,,
Maltose	54·84 ,,
Glucose and Lævulose	2·33 ,,

It can be seen that its main constituents are maltose and dextrin. There is present usually also some diastase, the quantity depending on the care taken in the preparation of the extract. Malt extract is used for the improvement of bread. The maltose provides sugar for the yeast, thus quickening fermentation, whilst the dextrin, being of a gummy nature, serves to keep the bread moist.

Green malt is also extracted with cold water, filtered, and the extract is evaporated at a low temperature in vacuo to a paste. The product is the commercial article termed "diastase paste." By the cold water extraction the action of the diastase on the starch takes place only to a very limited extent. Thus the important constituent of the paste is the enzyme *diastase*. The following values show the composition of an average "diastase paste":

Water	24·50 per cent
Mineral salts	0·95 ,,
Dextrin	8·11 ,,
Proteins	3·84 ,,
Reducing sugar (calculated as maltose)	62·60 ,,

Diastase paste, used at the rate of about 1–1½ lb. per sack of flour, improves the loaf generally. Best results are obtained with strong flours rather than weak flours; these latter, as a rule, have a good gas-producing capacity. The diastase paste provides sugar from the starch and the sugar is employed by the yeast in gas production. It is claimed also that the bloom crust, volume, and general appearance are all improved by the use of a diastase paste.

Properties of Maltose. When pure it exists in white needle-shaped crystals, and is easily soluble in water and moderately sweet to the taste. It is only fermented by yeast after con-

version to dextrose, but it readily reduces Fehling's solution. It has a dextro-rotatory power, i.e. its solution rotates the plane of polarised light to the right.

Sugars in Wheat and Flour. Both maltose and cane sugar are present in wheaten flour. At least, there is present 1·0–1·25 per cent of a sugar with properties similar to those of cane sugar, i.e. a sugar which does not reduce Fehling's solution until after hydrolysis. If a cold water extract of a flour be made and filtered, it is possible to show the presence of a reducing sugar in the extract by means of Fehling's solution. The reducing sugar in question is maltose. Whether all the maltose was originally present in the wheat grains is difficult to say, since aqueous infusion will promote, to some extent, the action of the enzyme diastase on the starch, and some may be produced during conditioning. The maltose may be estimated by extracting a known quantity of flour and treating an aliquot portion of the filtrate with Fehling's solution. The cuprous oxide produced is weighed and the maltose corresponding to it is calculated. If then another aliquot portion of the filtrate be hydrolysed by boiling with hydrochloric acid and then neutralised, it is found that the weight of cuprous oxide (red oxide of copper) produced on treatment with Fehling's solution is more than in the first case, i.e. more than corresponds to the maltose alone. The difference in the two weights represents the cuprous oxide corresponding to the " invert " sugar produced by hydrolysis, presumably of cane sugar. Standard conditions must be adopted for sugar estimations, since the aqueous extracts of flours contains enzymes which are capable of converting starch to sugar during the period of extraction. (An extraction for 1 hour at 27° C. is commonly employed.) Maltose is present in flour to the extent of about 1·7–1·8 per cent, whilst the sugar which reduces Fehling's solution only after hydrolysis is present to the extent 1·0 1.25 per cent.

The Polyhexoses or Polysaccharides. These include, as their name implies, the more complex carbohydrates, e.g. starch, dextrin, and cellulose.

Dextrin. This name is given to a body (or rather a number of bodies) simpler in constitution than starch, but yet very complex, and produced from starch by either heating alone

or with certain reagents. Dextrin may be prepared commercially by moistening starch with a trace of nitric acid, drying and then heating to a temperature between 150°–200°. Various coloured products are obtained according to the temperature employed; these are dextrines, differing in complexity. Water dissolves dextrin to give a gummy solution. The dextrin is said to exist in the *Colloidal State.** Solutions of dextrin are used commercially under the title "British gum," for adhesive purposes.

Dextrin is precipitated from aqueous solution by alcohol, a fact employed in estimating dextrin in the presence of maltose, etc. Aqueous solutions of dextrin are strongly dextro-rotatory, hence its name. Solutions of commercial dextrin reduce Fehling's solution, but this is stated to be due to the presence of reducing sugars, the pure dextrin being without action on Fehling's solution. Likewise dextrin is not fermented by yeast. With iodine, either a reddish brown colour or none at all is obtained, according to the constitution and complexity of the dextrin. This fact enables it to be distinguished from starch, which gives an intense blue coloration with iodine. Dextrin is produced on the crust of a loaf of bread when baked. It is this dextrin which gives glaze to the surface of the loaf.

Starch. Starch is widely distributed in the vegetable kingdom. It is stored up by many plants as a reserve supply of food, in the seeds of cereal plants and in the tubes of the potato, dahlia, etc. The starches obtained from any of these sources are the same chemically, but differ markedly in their physical character. If examined by the naked eye, starch is found to be a white granular powder. If, however, it be examined under a microscope, it is found to be possessed of a definite cell structure. Each cell consists of an outer covering of "starch cellulose" enclosing the substance which may be termed "starch proper"—or "amylose."

The size and shape of the starch cells vary according to the source from which they are derived. Each starch has a microscopic appearance sufficiently characteristic to enable it to be identified by that appearance. Moreover, since this is practically the only difference in the starches, it forms a

* See page 174.

valuable means by which adulteration may be detected; either adulteration of one starch with another or a flour with another, e.g. potato or rice starch grains are markedly different from those, say, of wheat, so that starch from either of these two sources could be readily detected in wheat-flour by a microscopic examination.

Microscopic Characteristics of a Few Common Starches.

To examine a starch or flour microscopically, the following procedure is adopted. A small quantity of the starch is placed on a clean microscope slide, a few drops of water are added to form a slight milky suspension, and the whole is covered with a cover glass carefully, so as to exclude all air bubbles. Surplus water is absorbed by a piece of filter paper,

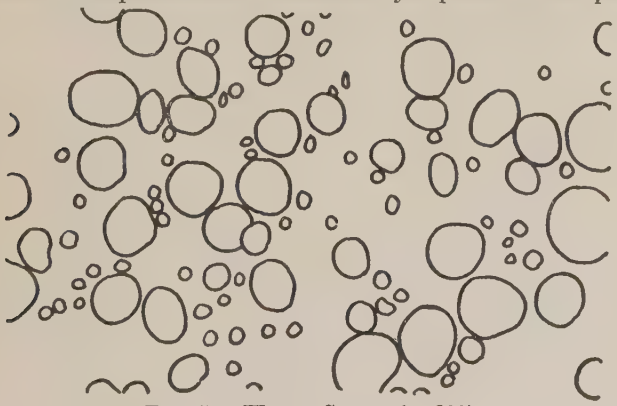


FIG. 47.—WHEAT STARCH (× 300)

and the slide is then ready for examination. It should be noted that a specimen mounted in this way will not last indefinitely, since the specimen slowly dries up. To make permanent mountings, glycerine jelly may be employed and the cover glass is sealed with a coating of varnish.

Wheat Starch may readily be obtained from wheat flour by making the latter into a dough, enclosing this in a silk or muslin bag, and kneading gently under water. The starch particles pass through the muslin, leaving behind a mass of gluten. If necessary the starch may be allowed to settle, filtered and air-dried.

Viewed under the microscope, wheat starch appears as a number of circular cells (Fig. 47). These are variable in size, but mostly of an average diameter of ·006 mm. or of ·05 mm. Medium-sized cells are present in comparatively few numbers. Occasionally, a cell may be viewed edgewise, when it will be seen to be lenticular in shape. Old samples of flour or starch show cracks and fissures in the cell walls.

Potato Starch. This may be obtained by scraping a freshly cut potato into a pulp and treating this in a muslin bag just as for wheat flour. On examination under a microscope the cells are found to vary greatly in shape and size (Fig. 48);

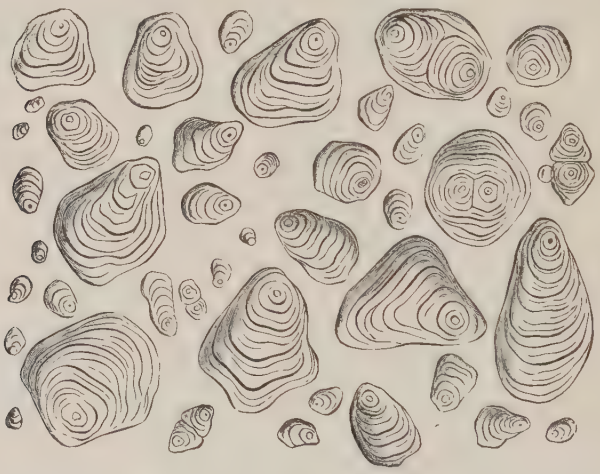


FIG. 48.—POTATO STARCH (× 300)

the larger cells are mainly oyster-shaped, with characteristic concentric ring markings. In the narrow end of the cell is to be observed a dark spot termed the "hilum." The concentric rings surround this hilum, being closer together at the narrow end of the cell than at the wider end. These large cells are larger than those of wheat, having an average diameter of ·07 to ·10 mm.

Rice Starch. Rice starch cells are characterised by being very small in size, and angular in shape (Fig. 49). The cells

are usually 5- or 6-, but sometimes 3-sided. Average diameter ·004 to ·006 mm. Often a number of cells are to be seen clustered together to form a larger aggregate.

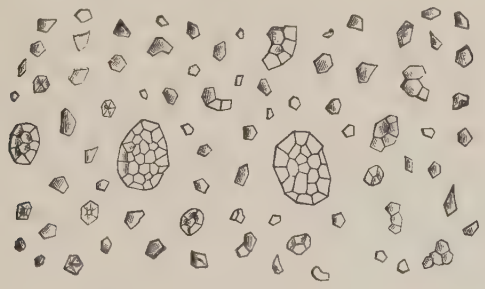


FIG. 49.—RICE STARCH (× 300)

Barley Starch. This bears a close resemblance to wheat starch, the large grains being slightly smaller than those of

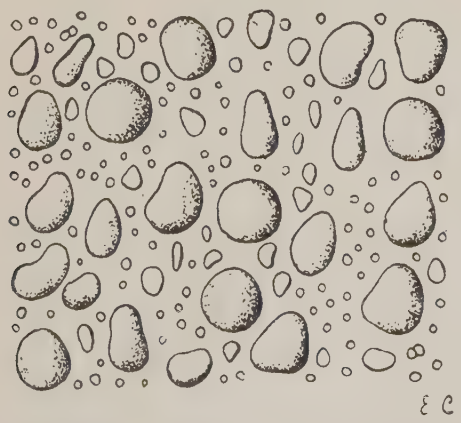


FIG. 50.—BARLEY STARCH (× 300)

wheat, the average diameterbeing ·018 to ·025 mm. Whilst most wheat starch grains are circular, those of barley show a tendency to bulge on one side.

Properties of Starch. Starch is a white, inodorous, granular powder; if squeezed between the fingers a peculiar "crunching" sound is heard, presumably due to the cells slipping on one another. It has a density of 1·55–1·60, and is extremely hygroscopic, i.e. absorbs moisture from the atmosphere. Ordinary air-dried starch usually retains about 18 per cent water, which can be driven off in a current of dry air at a temperature of 110° C. The anhydrous starch so produced again readily absorbs water when exposed to air. If starch be heated to temperatures above 110°, it commences to decompose, *moisture of constitution* being lost; at first dextrins are produced, but finally it chars and leaves a mass of carbon.

Starch is usually stated to be insoluble in water. Actually, cold water has no effect on it, since the outer cellulosic covering of the cell protects the starch proper. The cellulose covering is insoluble in water and most other solvents; thus starch does not dissolve unchanged in any liquid. If, however, the cell wall be ruptured by some means, then the amylose will dissolve in water to give a kind of solution. (Actually a colloidal solution. See Chapter XIII.)

By the action of hot water, the cells swell and burst, the contents dissolving to give a thick, gelatinous, somewhat cloudy solution. This process is described as the "gelatinisation" of starch and occurs at slightly different temperatures for starches from different sources. From this "solution" of starch the addition of alcohol causes the precipitation of a white amorphous powder which is amylose; this substance is structureless and easily dissolves in cold water.

If starch be treated in the cold with dilute acid for several days, it undergoes a peculiar change. It loses its power of gelatinisation and dissolves in water to form a limpid solution. Such starch is termed "soluble starch."

If heated with dilute acids, starch first yields maltose and dextrin, but continued heating results in the formation of glucose:

$$\underset{\text{starch}}{2(C_6H_{10}O_5)} + H_2O = \underset{\text{maltose}}{C_{12}H_{22}O_{11}}$$

$$C_{12}H_{22}O_{11} + H_2O = \underset{\text{glucose}}{2C_6H_{12}O_6}$$

Similar reactions take place with certain enzymes. (See Chapter XIII.)

The enzyme diastase which is present in malt flour or diastase paste is capable of converting starch to maltose and dextrin :

$$\underset{\text{starch}}{6(C_6H_{10}O_5)} + 2H_2O \xrightarrow{\text{diastase}} \underset{\text{maltose}}{2C_{12}H_{22}O_{11}} + \underset{\text{dextrin}}{2(C_6H_{10}O_5)}$$

This reaction may be quite readily demonstrated in the laboratory by starting with starch paste. This has the property of forming an intense blue coloration with an aqueous solution of iodine in potassium iodide. This blue colour, which vanishes on heating and reappears on cooling, is attributed to the formation of a loose compound referred to as " starch iodide." This reaction is extremely delicate and reveals minute traces of either starch or iodine.

If, then, starch paste be added to some malt flour and kept at a temperature of about 20–30° for 1 hour, the diastase converts starch to maltose and dextrin. When the reaction is finished, the liquor will give no blue colour with iodine, but will reduce Fehling's solution due to maltose present. Starch paste has no reducing properties at all.

The enzyme *pytalin* which is present in the saliva has the same saccharifying effect on starch.

Owing to its complex colloidal character, it is practically impossible to determine the molecular weight of starch. It has been computed, however, that it is in the neighbourhood of 32,400, which would give a formula to starch of $(C_6H_{10}O_5)_{200}$. The simplest or empirical formula $C_6H_{10}O_5$ is, however, used throughout this book.

Cellulose $(C_6H_{10}O_5)_n$. Cellulose is the principal component of the cell walls of plants. It constitutes the framework or skeleton of all vegetable tissues. There are many physical modifications of cellulose, varying from the hard woody fibres of wood to the delicate cellulosic covering of starch cells. Linen, cotton, wool, and certain kinds of paper, after treatment with mineral acids, yield a product which is almost pure cellulose.

Pure cellulose is insoluble in most solvents. It dissolves however, in an ammoniacal solution of copper hydroxide, and also in caustic soda in the presence of carbon disulphide. From either of these solutions cellulose is reprecipitated by acids.

A variety of changes occur when cellulose is treated with an acid or alkali, according to the concentration of the reagent. Nitric acid, in the presence of sulphuric acid, converts it to nitro-cellulose or gun-cotton, whilst fuming nitric acid oxidises it to oxalic acid $\begin{matrix}\text{COOH}\\|\\\text{COOH}\end{matrix}$

Paper, dipped momentarily into a diluted sulphuric acid solution, is converted to a tough parchment-like material. Cold concentrated sulphuric acid dissolves cellulose slowly, and on dilution and boiling, reducing sugars are formed.

Boiling solutions of 5 per cent sulphuric acid or alkali have little or no effect on the forms of cellulose present in the branny coats of wheat, and this fact is employed in estimating the cellulose or "crude fibre" content of a sample of offal. The cellulose present in wheat grain may be divided into three forms:

(*a*) The woody cellulose or fibre constituting the bran. The human system cannot digest and assimilate this cellulose, which has no nutritive value whatsoever for human beings. In white flour this woody cellulose has been completely removed in the milling operations. It is present, of course, in wholemeal flour and bread, where it acts as "roughage" during the digestion processes.

(*b*) The "parenchymatous" cellulose which divides the endosperm into sections. This delicate form of cellulose is more or less readily attacked by chemical reagents.

(*c*) "Starch cellulose" is the covering of the individual starch cells. This also is readily attacked by chemical reagents. It may be observed in thin starch pastes, but by treatment with boiling dilute acid a perfectly clear solution is obtained, containing, of course, the products of the hydrolysis of the starch.

The woody cellulose or fibre of the wheat grain acts as a protective coating to the delicate grain. What is usually termed the "bran" can be divided into a number of coatings:

(*a*) The outer envelopes of the grain, consisting of three layers; the epidermis, the epicarp, and the endocarp. This latter layer is characterised by well-marked cells almost round in shape. This outer envelope comprises about 3 per cent of the whole grain.

(*b*) The "testa" or episperm, beneath which lies a thin membrane. The bulk of the colouring matter of the bran resides in the testa, which encloses the whole grain. The testa and membrane together comprise about 2 per cent of the whole grain.

(*c*) The "aleurone" cells. These cells, which contain a protein termed "aleurone," terminate at the junction of the endosperm and germ. The cells have a characteristic square outline, and are quite easily seen in a microscopic view of a longitudinal section through a wheat grain. Of these three branny coats (*a*) consists almost entirely of cellulose, (*b*) less cellulose, but with some colouring matter, whilst (*c*) contains only a skeleton of cellulose filled with protein (aleurone). This protein must not be confused with the gluten of the endosperm which is included in flour manufacture, whilst the branny coats (*a*), (*b*), and (*c*) are rejected. These rejected products still contain adhering portions of endosperm and are used as feeding stuffs for cattle, etc.

The estimation of crude fibre or cellulose in wheat products has recently assumed some importance owing to an order requiring millers to declare the fibre content of their offals. The order referred to is "The Fertilisers and Feeding Stuffs Regulations, 1928"* which requires that the limit of variation in the fibre content of wheat offals or millers' offals, shall be one-eighth of the amount of fibre declared, i.e. if a sample of offal is declared as containing 8 per cent fibre, then the actual fibre content must not vary by more than 1 per cent, and must be between 7 and 9 per cent.

The methods of analyses are also prescribed. That for the determination of fibre is as follows:

"2-3 gm. of the sample, accurately weighed, shall be extracted with petroleum spirit (B. Pt. 40–60° C.) in an extraction apparatus,† or at least three times by stirring, settling, and decantation, and the dry residue transferred to a conical 1,000 millilitre‡ flask. The material must not be further ground during extraction. A volume of 200 millilitres of a solution containing 1·25 gm. of sulphuric acid (H_2SO_4)

* His Majesty's Stationery Office, Kingsway, London.

† The extraction of fat is necessary, otherwise erroneous results are obtained.

‡ 1 millilitre = $\frac{1}{1000}$ part of a litre and is almost equal to 1 c.c.

per 100 millilitres measured at ordinary temperature and brought to boiling point, shall be added to the flask and heated. The contents of the flask must come to boiling within 1 minute and the boiling throughout must be gentle and continuous for exactly 30 minutes, the original volume being maintained. The flask shall be rotated every few minutes in order to mix the contents and remove particles from the sides. At the end of 30 minutes the flask shall be removed and the contents poured at once into the shallow layer of hot water remaining in a funnel fitted with a pump plate or alternatively into a similar layer remaining in a Buchner funnel. The funnel shall be prepared by cutting a piece of cotton cloth or filter paper to cover the holes, so as to serve as a support for a disc of ordinary filter paper; boiling water shall be poured into the funnel and allowed to remain until the funnel is hot, whereupon suction is applied. The experiment shall be discarded if the time of filtration of the bulk of the 200 millilitres exceeds 10 minutes. The residue shall be washed with boiling water until the washings are free from acid. The residue shall then be washed from the filter paper back into the flask with a volume of 200 millilitres of a solution of sodium hydroxide, containing 1·25 gm. of NaOH per 100 millilitres free or nearly free from sodium carbonate, measured at ordinary temperature and brought to boiling point. The contents of the flask shall be boiled for exactly 30 minutes, the precautions given for the treatment with acid being observed. At the end of 30 minutes the flask shall be removed and its contents immediately filtered through an ordinary filter paper. The residue collected on the filter paper shall be washed with boiling water, then with a 1 per cent solution of hydrochloric acid and again with boiling water till free from acid. The residue shall then be washed twice with 95 per cent alcohol and three times with ether. The residue shall then be transferred to a dried weighed ashless filter paper, dried at 100° C. in an oven and weighed in its weighing bottle till constant in weight. The ash of the paper and contents shall be determined by incineration at a dull red heat. The weight of the ash shall be subtracted from the increase in weight found on the paper and the difference shall be reported as fibre." Before the fibre content of a sample is determined it is also desirable that

it be dried at 100° C. Thus the fibre content is determined on the dried, fat-free material.

Kent Jones * gives the following average values for fibre content in various milling products :

(*a*)	Straight grade flour ..	·2 per cent
(*b*)	Patent flour	·25 „
(*c*)	Sharps	8·2 „
(*d*)	Bran	14·5 „

CHAPTER XIII

PROTEINS—COLLOIDAL STATE—ENZYMES

THE PROTEINS

The group of compounds termed *proteins* play an extremely important part in the life processes of animals and plants. Various terms have been employed to signify this group of bodies, viz. *proteins*, *proteids*, and *albuminoids*. Owing to confusion arising from the use of all these terms, a committee of scientific societies recommended in 1907 the abolition of the word *proteid*, the use of the term *protein*, and that the use of the word *albuminoid*, as a general name in connection with these bodies, be discouraged.

In spite of these recommendations, the name albuminoid is still applied to these bodies, particularly by trade journals and government publications.

Proteins are essential to the growth of all animals and plants. They are commonly divided into two groups according to their origin : (*a*) animal proteins, (*b*) vegetable proteins.

Animal proteins are present in such things as muscle, blood, milk, where they are derived from vegetable proteins taken as foodstuff. It is characteristic of animals that they are unable to synthesise proteins, which are complex nitrogenous compounds, from simple inorganic nitrogenous compounds. All animal proteins are derived, directly or indirectly, from other animal sources, or from proteins of the vegetable kingdom. Plants, on the other hand, are able to build up

* *Modern Cereal Chemistry.*

proteins from simple inorganic compounds, like ammonia or nitrates ; one group of plants, viz. the pulses, comprising the bean and pea, are even able to assimilate free nitrogen from the atmosphere and build this up into complex compounds. This, they are enabled to do by reason of a parasitic micro-organism on their roots. Ordinarily, plants derive these simple nitrogen compounds from the soil. It is necessary when a patch of soil becomes depleted of these vital components, to replace them by applying manures or artificial fertilisers.

Composition and Constitution of Proteins. Proteins are characterised by containing always nitrogen, and sometimes sulphur, in addition to the usual elements comprising organic compounds, namely, carbon, hydrogen, and oxygen. They do not differ markedly in their percentage composition. All are exceedingly complex and of high molecular weight. They are colloidal in nature and cannot be obtained in crystalline form ; hence they are difficult to purify.

Of recent years, Emil Fischer, a distinguished German chemist, has shown that the protein molecule is built up of a series of amino-acids. He has, further, synthesised or built bodies very like proteins by condensation of various amino-acids.

Proteins in their properties are very much alike and are not therefore easy to separate from one another in the isolation from the parent source. In a general way the following properties may be ascribed to them :

Physical Properties of Proteins.

(1) They are colloidal in nature and do not diffuse through animal membranes. Some are soluble in water, others are not : some dissolve in weak saline solutions, whilst all are insoluble in absolute alcohol and ether.

(2) Some proteins are coagulated by heat or alcohol under various conditions, the coagulated material often losing the property of redissolving, e.g. egg albumin and globulin from wheat.

(3) All are optically active, all being lævo-rotatory.

(4) They are precipitated to various extents by salts, e.g. NaCl, $MgSO_4$, $(NH_4)_2SO_4$. The precipitation is purely physi-

cal, and the precipitate can easily be redissolved, e.g. a saturated solution of ammonium sulphate precipitates all proteins.

Chemical Properties of Proteins.

(1) On being heated the nitrogen is evolved as ammonia, usually accompanied by a smell of burnt hair.

(2) They yield various colour reactions which are useful for detecting proteins, e.g. with nitric acid, Millon's reagent.*

The more important vegetable proteins may be classified as follows :

Simple Proteins.

(*a*) *Albumins.* Soluble in water, or half saturated ammonium sulphate solution, coagulated by heat. The best known vegetable albumin is *leucosin* from wheat. Leucosin may be extracted from wheat flour with cold water : it is incompletely coagulated at about 52° C. and is present to the extent of 0·3 per cent of the whole grain.

(*b*) *Globulins* are insoluble in water but soluble in dilute salt solutions. They are precipitated by saturation with sodium sulphate at 33° C., e.g. an unnamed globulin from wheat present to the extent of 0·6–0·7 per cent of the whole grain.

(*c*) *Glutelins* are insoluble in neutral aqueous solutions and 70 per cent alcohol ; soluble in very dilute acids or alkalis. The best known member of this group is *glutenin* from wheat, one of the constituents of gliadin. It is present in wheat to the average extent of 7·75 per cent of the whole grain.

(*d*) *Prolamins* or alcohol soluble proteins. These are soluble in 70–80 per cent alcohol. The best known member of this group is *gliadin* from wheat, the second constituent of gluten. It is present usually to the extent of 4·3 per cent of whole grain. Gliadin is also present in rye.

(*e*) *Albuminoids.*

(*f*) *Histones.*

(*g*) *Protamines.*

These latter proteins are unimportant in connection with wheat.

* For details consult any standard work on " Biochemistry." The reactions are also given in Jago's *Technology of Bread-making.*

In addition to these simple proteins, complex *conjugated proteins*, containing sulphur and phosphorus, and *derived proteins* are known. The latter include the *proteoses*, which are produced by the partial hydrolysis of proteins and of which there is present in the wheat grain a small proportion (about 0·3 per cent). The gliadin and glutenin are the important proteins of wheat, since these form what is commonly termed *gluten*.

Wheat flour, on being moistened with water, can be formed into an elastic mass termed "dough." If this be treated in a silken or muslin bag under water, starch passes through the bag and settles out in the water. There remains behind a sticky, elastic mass termed "crude gluten." This consists largely of a mixture of gliadin and glutenin, together with traces of other constituents of the original flour. It is from the quality (elasticity, coherence, etc.) and to a lesser extent the quantity of this gluten that the baking qualities of the flour may be approximately gauged.

Wheat flour is unique in containing these two proteins, gliadin and glutenin, in such proportions to form this elastic body termed gluten. It is the presence of this gluten that enables us to make that light porous mass which is termed bread. Gas bubbles are produced in the doughy mass during fermentation in bread-making; the bubbles distend the dough, whose elastic properties enable it to retain the gas and its expanded aerated form until the heat of the oven changes the physical character of the mass so as to fix the dough as a solid. Without the aeration or without the gluten, a flat, biscuit-like material is produced.

Many attempts have been made in the past to discover why it is that some flours yield good loaves and others poor ones. By a good loaf is meant "a bold, well-risen loaf of uniform texture." Attention was early directed to the gluten as being one of the factors affecting the bread-making qualities of a flour. Likewise it was early recognised that the quantity of gluten was of far less importance than the quality (i.e. elasticity, coherence, etc.) of the gluten. Many investigations have been carried out concerning the quality of gluten, and of recent years with increase in our knowledge of the "colloidal state" it has been generally recognised that the problem is a colloidal one. The physical condition of the gluten is

influenced by the nature of its surroundings, and it is from an examination of these surroundings (e.g. the presence or absence of various salts, the concentration of hydrogen ions *) in a flour of good baking quality, that we are enabled to imitate them in a poorer quality flour, in order to modify favourably the physical condition of the gluten. This is virtually what happens when "improvers" are added to flour.

Properties of Gluten. As washed out from flour, gluten is a sticky elastic mass. Glutens from weak flours, e.g. English, are usually runny with little or no coherence, whilst those from strong flours are coherent masses, capable of being stretched to two or three times their own length without breaking. The mode of washing, temperature, etc., influences the quantity of gluten within small limits, hence many workers have abandoned this method of arriving at the gluten content of a flour in favour of a determination of the nitrogen and use of a factor. The gluten obtained by washing is often weighed wet and the value given as "wet gluten." Thus the percentage of "wet gluten" varies from 40·5 per cent in a strong flour to 30·5 per cent in a weak one.

If the moist gluten be dried in an oven at 100°, the resulting mass is a hard, brown brittle material, which does not absorb water to reproduce the elastic mass. Although the ratio of wet to dry gluten is often 3 : 1, it is by no means constant. Thus the percentage of dry gluten in the examples given above were 13·5 per cent and 11·1 per cent respectively. This dried gluten, which is substantially a mixture of gliadin and glutenin, contains traces of other products from the original flour, and hence is not a true guide to protein content, e.g. an analysis of dry crude gluten shows the following contents : †

Ether extract (fat)	4·20 per cent
Carbohydrates, not fibre	9·44 „ „
Fibre	2·02 „ „
Mineral matter	2·48 „ „
Gliadin	39·09 „ „
Glutenin	35·07 „ „
Globulin (10 per cent NaCl extract)	6·75 „ „
	99·05 per cent

* See Appendix. † F. A. Norton, *J. Amer. Chem. Soc.*, 1906, 28, 8–25.

Thus the crude gluten may be regarded in the light of the above figures as about 75 per cent true gluten.

The determination of true gluten in a sample of crude gluten may be made without actually separating the gliadin and glutenin by determining the nitrogen content of the material by a Kjeldahl estimation. Then, since the nitrogen contents of gliadin and glutenin are approximately the same (17·60 per cent), the protein may be found from the nitrogen by multiplying by a factor $\frac{100}{17{\cdot}6} = 5{\cdot}68$, i.e. percentage of protein = percentage of N $\times$ 5·68.

COLLOIDAL STATE

Thomas Graham (1805–69) classified substances, according to their behaviour in aqueous solutions, into two classes: (*a*) those which would diffuse or pass through an animal membrane, e.g. parchment, and (*b*) those which did not diffuse through an animal membrane. To the first, he gave the name *crystalloids*, since they were usually substances of a crystalline character, like common salt, and to the second he gave the name *colloids*. In this second class were found bodies of a non-crystalline or sticky, gelatinous nature like silicic acid or glue, gum, starch. Moreover, Graham devised a method of separating bodies of the two classes. If an aqueous solution containing a mixture of, say, gelatine, salt, and sugar be confined in a sac of parchment (Fig. 51, a), and the whole placed in a second vessel of water, the sugar and salt diffuse through the membrane into the water, whilst the gelatine remains behind. Such a process is termed *dialysis*, and is employed for the purification of proteins, which are colloidal substances.

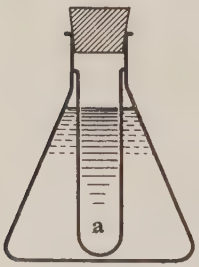


FIG. 51

Since the time of Graham, however, the meaning of the

term "colloid" has undergone a modification, and to-day the term is applied not to a class of bodies but to a state of existence. We speak of a substance as occurring in the colloidal state rather than as a colloid, since it has been shown that practically any substance may be brought into the "colloidal state" by employing suitable conditions; even such normally characteristic crystalline substances as common salt have been produced in a colloidal state. If the theory of colloidal state be examined it will be found that the real difference between a substance in a true solution and a colloidal solution, or in a suspension, is merely a difference in size of particle.

If we compare the three states: (1) a suspension, say of sand particles in water, (2) a colloidal solution of starch in water, and (3) a true solution of common salt in water, it will be found that the sand particles are of such a size that they will readily settle out of the liquid, or in any case are much larger than the pores of an ordinary filter paper, so that they can be filtered out by a filter paper, whilst the particles in the colloidal starch solution are of such a size that they will pass through the pores of an ordinary filter paper, but *not* through the pores of an animal membrane, say parchment, and the particles of common salt are so minute that they will pass either through paper or through parchment. Moreover, the sand particles are of such a size that they can be seen with the naked eye, whilst the presence of colloidal particles can be revealed by a device termed an "ultra-microscope," and the salt particles cannot be made apparent by any known means. Thus it will be seen that from the point of view of particle-size, substances in the colloidal state are intermediate between those in a suspension and those in a true solution. The general average size of particles in the three states is as follows:

Suspensions,	greater than $\cdot 1\mu$*	i.e. $\cdot 0001$ mm.
Colloidal solution,	$\cdot 1\mu$ to $1 \cdot 0\mu\mu$	i.e. $\cdot 0001$ mm. to $\cdot 0000001$ mm.
True solution,	less than $1 \cdot 0\mu\mu$	i.e. $\cdot 0000001$ mm.

These three systems may be described as *disperse systems*, the

* The units commonly employed in microscopic measurement are: (1) the micron $\mu = \frac{1}{1000}$ mm.; (2) the sub-micron $\mu\mu = \frac{1}{1000000}$ mm.

solid being " dispersed " in the solute. Thus of the three substances exhibiting varying degrees of dispersion, the sand possesses least degree of dispersion, whilst in the colloidal state the solid is more highly dispersed and the salt exhibits the greatest disperson of all three. It must be borne in mind that this dispersion is merely a matter of degree ; even among the substances in colloidal state different degrees of dispersion are to be observed. The limits of dispersion in the colloidal state are fairly wide.

Liquid colloidal solutions are termed *sols*, whilst when a sol is coagulated, thereby diminishing the degree of dispersion, a jelly-like material is produced, termed a *gel*. If the degree of dispersion be even further diminished, e.g. when dehydration occurs, a solid termed a dried-up gel or *coagel* is formed. Complete dehydration may result in a body which cannot be reconverted to a jelly by the addition of water. Such a gel is the wet gluten obtained from wheat. On complete drying it forms a hard horny mass which will not take up water again to swell and form an elastic mass. Gelatin, on the other hand, may be completely dried and yet, on the addition of water, swell up to form a jelly.

Protein (i.e. gluten) is present in flour in the form of a partially dried-up gel. There is on an average 15 per cent of water in flour. By some authorities, it is supposed that this partially dried-up gel has been produced during the ripening period of the wheat by the partial coagulation, and therefore reduction of degree of dispersion, of the proteins in the form of a sol, which rises in the sap of the wheat plant during its growth.

This partially dried-up gel has not lost its power of swelling to form a gel on the addition of water ; this happens when water is added to the flour to form a dough. The extent to which this swelling takes place, which is connected with the water-absorptive capacity of the flour, varies in different flours, and is dependent on the past history of the colloid, chiefly on the degree of dehydration which it suffered during the ripening period. Ripening may take place under some conditions such that the protein is little removed from the sol stage, whilst on the other hand in hot countries it may take place in such a way that the protein is dehydrated almost to the " irreversible " point, i.e. to the point beyond

which it is unable to absorb water and swell up into a doughy mass. Wheats ripened under the former conditions yield a flour which gives a gluten which is soft and runny, resulting in a dough which has poor gas-retaining qualities, e.g. English wheat, whilst a wheat ripened under the latter conditions will yield a flour with a tough, coherent gluten. In fact the gluten may be so tough that the gas produced during fermentation may be unable to distend the dough, e.g. Indian wheats. Such a flour is said to be "gluten bound." Flours vary between these two limits according to the characteristics of the wheats from which they were formed.

A further important feature of the colloidal state is the effect of the surrounding medium on the degree of dispersion. The presence of salts, acid (really hydrogen ion concentration), etc., has a marked effect on the physical condition of the colloidal substance.* Thus, if the colloidal condition of a flour be not correct for the production of a good loaf, it is possible to modify it and imitate the conditions of a good flour.

This is the object attempted when "improvers" are added to a flour. It is desired so to modify the physical condition of the gluten (i.e. its degree of dispersion) as to bring it into that condition which is best to form a good loaf. This, of course, assumes that there is a sufficiency of protein and also of gas to distend the dough.

ENZYMES

An enzyme may be thought of as an organic catalyst. It has been mentioned elsewhere that a catalyst is a body which influences the *rate* at which a chemical reaction proceeds. Some chemical reactions proceed rapidly and are complete almost instantaneously, e.g. the union of hydrogen and oxygen to form water, whilst others proceed only very slowly, e.g. the oxidation of ammonia to nitrogen peroxide. The rate may even be so slow as to be almost imperceptible. A catalyst increases the *rate* at which a reaction proceeds without affecting the nature or the quantity of the resulting products; thus in the oxidation of ammonia to nitrogen peroxide by air, red-hot platinum is used as a catalytic

* See Wood, *Story of a Loaf of Bread.*

agent. This platinum, as far as we know, suffers no change itself and all remains after the reaction is complete. The hydrolysis of cane sugar to form glucose and fructose by boiling with diluted sulphuric acid is another example of catalysis. The sulphuric acid is the catalytic agent and remains unchanged after the hydrolysis is completed. Enzymes play a similar part in organic chemistry in that small quantities of them are able to bring about profound chemical changes in relatively large amounts of material. Enzymes are elaborated by, and found associated with, living organisms, but are quite able to function apart from the living organisms, e.g. the enzyme " diastase " is elaborated by certain cereals during germination, and the enzyme " zymase " is produced in the yeast cell, but is quite able to act when freed from the living cell. The general characteristics of enzymes are as follows :

(1) They are colloidal in nature, and hence are difficult to isolate pure. Preparations containing them are, however, comparatively readily obtained.

(2) They are extremely complex in chemical constitution and usually contain nitrogen. No formula has as yet been arrived at for any of them.

(3) They are specific in their action, i.e. one enzyme is capable of bringing about only one chemical change. i.e. those enzymes which hydrolyse starch will do that and nothing else.

(4) They function at their best under certain definite conditions of temperature, and their action is often destroyed by elevated temperatures. Diastase exhibits its maximum activity at 65° C.

Classification of Enzymes. The most important from the point of view of a student of flour milling are the following :

(1) HYDROLYTIC ENZYMES.

(*a*) Carbohydrate splitting enzymes.

Invertase is present in yeast cells and hydrolyses cane sugar to dextrose and lævulose.

Maltase is present in yeast cells and hydrolyses maltose to glucose.

Diastase. It is probable that there are two enzymes which are usually included under this heading : (1) that which converts starch paste into soluble starch, i.e. liquefies the starch ; this is present in malt and prepara-

tions derived from malt, and (2) that which saccharifies the starch, i.e. hydrolyses the starch to maltose. This is present in small quantities in raw grain, either barley or wheat.

Ptyalin. Present in saliva ; saccharifies starch.

(*b*) Protein splitting enzymes (proteolytic enzymes).

Protease. Splits up proteins into simpler bodies ; present in malt extract which is often employed to soften or mellow a harsh gluten.

(2) Fermenting Enzymes.

(*a*) *Zymase* is present in yeast cells and ferments sugar to alcohol and carbon dioxide.

(*b*) *Lactic acid ferment* is present in micro-organisms found in the air and converts lactose to lactic acid.

(*c*) *Butyric acid ferment* is present in micro-organisms found in decaying cheese and converts lactic to butyric acid.

(3) Cellulolytic Enzymes.

(*a*) *Cytase* is present in green malt and germinated wheat ; renders soluble the cellulose walls of grain. It is this enzyme which causes the solution of the parenchymatous cell walls in the endosperm of a wheat grain during germination.

Of these enzymes perhaps the most important one to be found in wheat is diastase. It is present in the germ of the grain, and the quantity increases if germination takes place. Most flours contain small quantities of diastase where its presence is of great importance. Its function is to convert starch to sugar (maltose), but as mentioned above possibly two enzymes are present, one which breaks down the starch cells and the other which hydrolyses the starch to maltose. The presence of diastase in flour results in the production of small quantities of maltose, which, along with a small quantity of a sugar with properties similar to cane sugar, forms the normal sugar content of a flour. It is this sugar which is acted upon by the yeast during the early stages of the fermentation of the dough forming alcohol and carbon dioxide. When this normal amount of sugar is exhausted, any further supplies must depend on the amount of diastase present. Thus, the amount of diastase present in a flour is intimately

connected with the gas-producing qualities of the flour, which is one of the main factors affecting the "strength" of the flour, i.e. the ability of a flour to yield a bold loaf of uniform texture. Flours with excessive diastase do not produce good loaves, e.g. flour from sprouted wheat which contains excessive diastase as a result of the germination. Flours, poor in diastase, may be improved by the addition of some diastase preparation, either malt flour or malt extract. The chief sources of diastase are the malt preparations, malt extract, malt flour and diastase paste (see under maltose). In malt extract, the reaction

$$\text{starch} \rightarrow \text{maltose}$$

has taken place, and the value of the extract lies in its maltose content. It still contains, however, small quantities of diastase. Malt flour is often added to a flour to improve its diastase content, and hence its gas-producing qualities. The ordinary methods of chemical analysis are inapplicable to the examination of enzymes owing to the impossibility of isolating them in a pure state. The activity of an enzymic preparation, e.g. the diastatic activity of a sample of flour, may be determined by examining its ability to convert starch to maltose. A known amount of the enzymic preparation is allowed to remain in contact with starch paste * at a known temperature for a definite time, at the end of which the amount of maltose present is determined by means of Fehling's solution.

It has been shown by Rumsey † that, using a patent flour from a hard wheat, and digesting 10 gm. of flour by itself for one hour at 27° C., the diastase produces about 0·3 gm. of maltose, whilst a straight run flour from a soft wheat under the same conditions produced only 0·034 gm. of maltose. Further, the former flour stood at the head of a list of flours in order of baking quality and the latter near the bottom. Thus it is fairly conclusive that the diastatic activity is one of the factors associated with the strength of a flour.

Fermenting Enzymes, Zymase and Alcoholic Fermentation. The specific function of zymase is the conversion of glucose

* Or alternatively no outside starch is used but the starch of the flour is acted upon by the diastase.

† American Institute of Baking, 1922.

to alcohol and carbon dioxide, a change usually referred to as alcoholic * fermentation.

Yeast is a micro-organism, i.e. a form of minute life, which grows and multiplies under suitable conditions, e.g. in dilute sugar solutions containing small quantities of nitrogeneous matter at slightly elevated temperatures. The yeast, to obtain food, attacks the glucose. In a sugar solution, small quantities of this are used up in enabling the yeast to multiply, which it does by "budding," i.e. a cell develops a "bud" which grows, eventually reaching the size of the parent cell, when it breaks off, forming an independent cell. The yeast cells elaborate enzymes, chiefly zymase, invertase, and maltose, as a result of their growth. This enables the yeast to break down the sugar, forming alcohol and carbon dioxide. The function of invertase is to convert cane sugar to glucose and fructose which then are acted upon by the zymase, and the maltase converts any maltose present to glucose, which again is acted upon by the zymase. Thus, whilst yeast will ferment glucose directly, in the case of cane sugar, inversion must first occur, and with maltose hydrolysis to glucose. Yeast will not ferment lactose and is also without action on starch.

It has been shown experimentally that if yeast be expressed, the yeast juice so obtained still has the power of fermenting sugar, though to a less extent. The yeast juice contains the enzymes which actually bring about the change. Two changes are going on during alcoholic fermentation: (1) the growth and multiplication of the yeast cells elaborating enzymes; (2) the decomposition of sugar by the enzymes, the latter being destroyed in the process. There is no accumulation of enzyme.

Fermentation by Yeast in Bread-making. Bread is commonly made by what is termed the "straight dough process," i.e. the requisite amount of flour, water, salt, and yeast are mixed together to form the dough. The time of fermentation varies according to the amount of yeast used, 8–10 hours being required when $\frac{3}{4}$ lb. of yeast per sack of flour is used, and about half that time when twice the quantity of yeast is used. The dough, having been made with warm water (about 35° C.). is allowed to ferment or

* A fermentation is a type of chemical change brought about by the life and growth of micro-organisms.

" prove " for $1\frac{1}{2}$ hours in a warm place (25° C.). During this period the original sugars in the flour are fermented by the yeast and the carbon dioxide produced distends the dough. At the end of this time the dough is well kneaded in order to expel the stale gas, and then allowed to ferment another half hour. The initial sugar content is rapidly used up and a further supply must be available if gas production is to continue. The extent to which this further supply is forthcoming depends on the diastatic activity of the flour. Sufficient maltose must be produced by the diastase in the flour to provide fermentable material for the production of gas after the original sugar is used up. Flours lacking in diastase will produce small loaves unless " improved " by the addition of some diastatic preparation. At the same time the gluten of the dough must be of such an elasticity to enable it to retain as much of the gas as possible. After moulding the dough into the required form, it is finally " proved " for a further thirty minutes and then baked for thirty minutes in an oven at a temperature of about 250° C. The total time taken over this " short dough " process is from 3–4 hours. In addition to the products, alcohol and carbon dioxide, as represented by the chemical equation :

$$\underset{\text{glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{ethyl alcohol}}{2C_2H_5{\cdot}OH} + \underset{\text{carbon dioxide}}{2CO_2}$$

small quantities of other products are produced at the same time, e.g. glycerol, succinic acid or traces of other acids. These products, though small in quantity, have an important effect (particularly the acidic bodies) in " ripening " the dough, i.e. influencing the physical state of the gluten so as to render it of a certain elasticity and toughness.

It is to this feature that the superiority of a yeast made loaf over an artificially aerated loaf is due. During the fermentation period, changes occur in the colloidal state of the mass, until finally the dough is placed in the oven, when a most profound change occurs. Further expansion occurs and the heat of the oven coagulates the colloidal particles, thus fixing the mass in a light aerated form. The alcohol produced during the fermentation is of course driven off and passes from the oven with the steam. In large bakeries the amount of alcohol so lost must be quite considerable, and it has been suggested that it might be worth while recovering it.

Lactic Acid Ferment. This has been mentioned previously under lactic acid. A micro-organism (*Bacterium lactis*), present in air and some yeasts, is capable of producing the chemical change :

lactose ——————→ galactose ——————→ lactic acid

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6 \longrightarrow 4CH_3{\cdot}CHOH{\cdot}COOH$$

This change occurs when milk is exposed to the air and becomes sour. Other common sugars may be similarly affected by the micro-organism.

The peculiar circumstances under which this micro-organism flourishes best are at a temperature of about 35° C. and in the absence of acid. Thus it will be seen that if left to itself a lactic fermentation will cease after a while owing to the formation of lactic acid. The lactic fermentation and alcoholic fermentation may go on in the same medium at the same time, unless precautions are taken to prevent the former.

In the fermentation of grape juice the liquor is sufficiently acid (tartaric acid) to prevent the lactic but to allow the alcoholic fermentation. Likewise in the manufacture of beers, the saccharine liquors are fermented at such a temperature that the lactic fermentation is inhibited and only the alcoholic fermentation allowed to proceed.

According to Jago, sour bread is the result of a combination of bacterial fermentation, principally that producing lactic acid. The principal causes of sourness are stated to be :

(*a*) Carrying the fermentation beyond the normal into the souring stage ;
(*b*) The use of vessels which are not scrupulously clean.

Authorities seem to differ as to whether the temperature in the oven during the baking of bread is sufficient to kill any micro-organisms that may originally have been present.

Acetic Acid Ferment has also been previously mentioned in connection with acetic acid. A micro-organism named by Pasteur *Mycoderma aceti* has the power of effecting the oxidation of alcohol to acetic acid. Like alcoholic fermentation, this change is brought about by an enzyme secreted by the organism, and which will function independently of it. The organism works best at a temperature of 33° C. and in a plentiful supply of oxygen. It is this organism which

effects the conversion of the alcohol in beer and wine to acetic acid during the production of vinegar.

Putrefactive Fermentation. Putrefaction may be described as the change which most organic (usually nitrogenous) compounds undergo with the production, first, of compounds having disagreeable putrid odours, and finally of simpler inorganic products. The chemical change brought about is the decomposition of, say, a complex nitrogenous compound into such simple products as carbon dioxide, hydrogen sulphide, hydrogen, nitrogen, ammonia, and the substituted ammonias, ethylamine and trimethylamine. The change is effected through the agency of micro-organisms present in the air and sewage, the chief of which are termed *Bacterium termo* and *Bacterium subtilis*. If substances of the nature of hay, meat, flour extracts be exposed to air under suitable conditions and afterwards examined microscopically they will be found to be crowded with micro-organisms. If left for sufficient length of time, these micro-organisms grow into colonies, visible with the naked eye.

Substances such as those named above may be prevented from putrefying in the following ways :

(*a*) By excluding air.

(*b*) By destroying any existing germs by suitable heat treatment. The germ-free material, which is said to be " sterile " or sterilised, will then keep indefinitely in the absence of air without showing signs of putrefaction. Tinned goods are possible owing to this fact.

(*c*) At low temperatures the power of putrefactive organisms is arrested ; thus meat may be kept in cold storage for quite considerable periods. On regaining normal temperature, however, the organisms again commence to exercise their functions.

(*d*) By drying or desiccating. Foodstuffs treated in this way will keep for long periods without showing signs of decomposition.

(*e*) By the use of antiseptics. Certain substances added in small quantities to foodstuffs produce a condition such that the putrefactive organism cannot develop and thrive in it, e.g. meat treated with a dilute solution of formaldehyde will keep for longer periods than meat not so treated. The

use of preservatives and antiseptics in foodstuffs is quite common, though restrictions have recently been imposed by the Food and Drugs Act, so that practically the only preservatives allowed in foodstuffs are sulphur dioxide and benzoic acid.

CHAPTER XIV

STRENGTH OF FLOUR—FLOUR IMPROVERS—BLEACHING OF FLOUR

STRENGTH OF FLOUR

THE "strength" of a sample of flour may be defined as its ability to produce a bold, well-risen loaf of uniform texture. It is well known that some flours produce only a small, badly aerated loaf; such a flour is said to be weak, whilst one producing a loaf with the characteristics quoted above is described as a strong flour. English flour may be taken as an example of the former and Manitoba flour of the latter.

It appears that there are two main factors which contribute to the strength of a flour:

(1) A factor controlling the size of the loaf.

(2) A factor controlling the shape or texture of the loaf.

Of these the first is concerned with the gas-producing qualities of the flour. The production of gas is again, of course, dependent on the sugars present, and also the ability of the flour to produce more sugar when the original amount present is used up, i.e. the diastatic activity of the flour. Thus, a certain diastatic activity to maintain a production of gas during fermentation to keep the dough fully distended, is one of the essential conditions of a strong flour. In certain anomalous cases an otherwise strong flour is lacking in diastatic activity; such a flour produces only a small loaf if baked by itself, but by assisting its diastatic activity the normal large loaf characteristic of a strong flour can be produced. It is for this reason that some authorities prefer to judge the strength of a flour, not on its loaf-making qualities, but on the behaviour of the dough. For a strong flour the dough should be tough and elastic and free from runnyness.

The second factor—the shape and texture of a loaf—is controlled largely by the physical condition of the gluten. In addition, a certain minimum quantity of protein must be present. In a strong flour the gluten is in a certain colloidal state, actually some definite degree of dispersion, such that, whilst being elastic enough to allow the doughy mass to expand, it must have sufficient tenacity to retain as much as possible of the gas produced. This particular desirable degree of dispersion of the gluten is dependent on the surrounding conditions, e.g. presence of salts, hydrogen ion concentration, etc. In a weak flour the gluten has little tenacity and elasticity, so that the gas bubbles escape from the doughy mass, leaving a small loaf, or bubbles of gas burst inside the dough to form larger bubbles, thus giving rise to a poor-shaped loaf of uneven texture. On the other hand, it is possible to have present a quantity of gluten which is too tough to allow the mass to expand. This may be overcome by the addition of malt extract which not only produces more gas to help distend the dough, but also contains proteolytic enzymes which tend to mellow the harsh gluten. These two factors might be combined, so that strength could be regarded as related to "gas retention," i.e. the power of the dough to retain the gas produced. If the production is poor, then the loaf will be poor, likewise if the retaining quality of the gluten be poor, even though gas production be high, the loaf will be poor. A flour deficient in either of these controlling factors may be improved, provided the nature of the deficiency is recognised.

Many attempts have been made to connect strength of flour with its chemical composition: these have yielded no results, and it is now fairly well understood that strength is largely dependent on the colloidal state of the gluten, i.e. provided a certain minimum quantity be present. Moreover, the colloidal state of the proteins is capable of being modified by modifying the character of its surroundings, and in "improving" a weak flour we aim at modifying the degree of dispersion of proteins so as to imitate that in a strong flour.

IMPROVERS

It is claimed for the substances used as improvers that they enhance the natural baking qualities of a flour by supplementing deficiencies or correcting conditions which impair its capacity for yielding loaves of the shape, volume, texture, and general appearance desired. The chief deficiency met with is a deficiency in gas production, and the condition which most often needs correction is the physical condition of the gluten. These variations are inherent in the character of the different wheats which are available to millers in this country. The use of improvers can be justified from commercial considerations in view of the facts,

(*a*) That it enables millers to produce a uniform product in spite of the variation in the characteristics of the wheats used in their mixtures.

(*b*) That it enables millers to use any supplies of sound wheat obtainable. It has been estimated that, were improvers disallowed, certain supplies of weak wheats could not be used and the output of the country would diminish markedly.

(*c*) That it enables more English wheat to be milled.

The chief agents employed as improvers are acid calcium phosphate, $Ca(H_2PO_4)_2$; acid ammonium phosphate, $(NH_4)\ H_2PO_4$; and ammonium persulphate $(NH_4)S_2O_8$.

In addition, extracts of malt and wheat germ are employed usually by bakers and other malt preparations by millers. Of these agents, acid ammonium phosphate, extract of germ, and the malt preparations are used primarily as yeast foods and to encourage yeast growth and gas production. Acid calcium phosphate, ammonium persulphate (in admixture with ammonium sulphate), together with the bleaching agents, chlorine and nitrogen trichloride, act chiefly in the direction of improving the quality of the gluten.

The Action of Improving Agents. If a flour be stored for several weeks it is found that not only does its colour tend to become whiter, but also its baking qualities improve. The process is referred to as the natural agency of flour.

It is practically impossible to bring about this improvement

in flour by storage in this country, owing to the lack of accommodation, and the increased cost to millers of carrying huge stocks of flour. Improvers aim at producing on newly-milled flour the effect of natural ageing. It is found that a flour on storing tends to increase its acidity. Actually, the acid produced appears to be a matter of doubt, but presumably the natural neutral phosphates of the flour are converted to acid phosphates (chiefly acid potassium phosphate). It has been shown by Wood that strong flours contain normally a high percentage of soluble phosphates as compared with weak flours, the acid phosphates of calcium and potassium are both more soluble than the corresponding normal phosphates. It would appear that to increase the acidity of a flour, and hence the acid phosphate, is to improve the flour. The improvement arises by reason of the fact that the acid phosphates play an important part in ripening the dough, i.e. getting the gluten into the most favourable elastic condition. During normal alcohol fermentation traces of acids (succinic acid, etc.) are produced which play a similar part. Acid calcium phosphate, $Ca(H_2PO_4)_2$, used at the rate of $\frac{1}{2}$ lb. per sack of flour, effects a great improvement in the loaf produced.* It acts both as a yeast food, promoting gas production, and on the gluten. It is one of the oldest improvers on the market; the criticism that improvers are chemicals foreign to flour cannot be levelled at acid calcium phosphate, since flour normally contains phosphates.

Acid calcium phosphate may be made commercially from bones ($Ca_3(PO_4)_2$) or other phosphate compounds by treatment with the calculated quantity of sulphuric or phosphoric acid:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaSO_4 + Ca(H_2PO_4)_2$$

The calcium sulphate is insoluble and can be separated from the phosphate. The presence of sulphate in commercial phosphate is usually small; in past years phosphates with quite appreciable quantities of sulphate were to be found on the market, hence the official recommendation restricting the maximum amount of sulphate to 10 per cent.† With the use

* A maximum of 3 per cent was specified by the National Association of Millers in evidence before a Departmental Committee set up to examine the question of bleachers and improvers in flour.

† Hamill, Local Government Board Food Reports, No. 13.

of sulphuric acid the possibility of the presence of traces of arsenic in the powder may arise. This matter is also the subject of a Local Government Board recommendation, though high-quality samples usually contain substantially less than the permitted limit ($\frac{1}{100}$ grain per lb.). With the use of phosphoric acid for producing high-grade acid calcium phosphate, these two impurities do not arise :

$$Ca_3(PO_4)_2 + 4H_3PO_4 = 3Ca(H_2PO_4)_2$$

The presence of acid calcium phosphate in a flour is readily detectable by the chloroform test for mineral matter (see Part I, page 70). In addition to the use of acid calcium phosphate as an improving agent, it is also used in the production of baking powders and self-raising flour. A self-raising flour is one to which has been added substances necessary to produce carbon dioxide on admixture with water and baking. Bread is made from such flours without the aid of yeast. The reagents employed to produce the carbon dioxide are usually cream of tartar (potassium hydrogen tartrate) or acid calcium phosphate mixed with sodium bicarbonate. In the presence of water interaction takes place with the liberation of carbon dioxide which distends the dough in the same manner as yeast (see Part I, page 60). Of recent years, acid calcium phosphate has largely replaced cream of tartar as the acid component of the mixture. A second important improving agent, which appears to be fairly extensively used is ammonium persulphate. One of the proprietary brands of improving agents consists of 25 per cent $(NH_4)_2S_2O_8$ and 75 per cent ammonium sulphate $(NH_4)_2SO_4$. The ammonium sulphate was originally used merely as a diluting agent, but it appears to act as a yeast food. The ammonium persulphate favours production of acid by the yeast during fermentation of the dough, and is recorded as having no effect on the production of gas.

Thus, it would appear that ammonium persulphate would be an eminently suitable improving agent for flours from wheats in which the gas production and enzymic activity are ample, but the proteins have not been sufficiently removed from the soil conditions during the ripening period to produce a tough-elastic gluten. The increased acidity during fermentation influences the physical state of the protein, possibly

by coagulation, an imitation of natural ripening, so as to bring it into correct condition for the production of a good loaf. Thus, ammonium persulphate improves the quality of loaves from English wheat but is useless for Indian wheats, in which the proteins are only just removed from the completely dried-up gel condition. In the presence of water, and during the fermentation period, ammonium persulphate decomposes, yielding atomic oxygen and ammonium hydrogen sulphate.* The small quantity of oxygen in this form is particularly active and may effect some slight bleaching. However, the resultant bread has a better texture than bread from untreated flour and this may be the cause of the white appearance of the bread. It will be seen also that no persulphate remains in the bread, the residue of sulphate resulting from the use of improver at the rate of one ounce per sack being exceedingly minute, and in any case sulphates are to be found normally in the ash from untreated flour. In addition to the two substances already dealt with, which are commonly used as improvers, the following may be mentioned :

Chlorinated Flour. In dealing with bleaching by chlorine, it will be seen that flour treated with chlorine is not only bleached but improved. Thus, a small quantity of heavily chlorinated flour, added to a flour requiring no bleaching itself, acts as an improving agent. The chlorinated flour is prepared by treating flour with chlorine, so that it absorbs about 5 to 6 lbs. of chlorine per sack of flour, and this is then used as an improver at the rate of 1 lb. per sack, when it is claimed that it produces a marked improvement in the loaf.

Potassium Bromate, $KBrO_3$. This substance, used at the rate of $\frac{1}{10}$ ounce per sack, acts as an improver. It is a neutral body, but a vigorous oxidiser. The mechanism of its use does not seem to be particularly clear.

Succinic Acid. This is one of the bodies produced during normal fermentation. Although its price prevents its use as an improver commercially, it is possible that many improvers act by causing the yeast during fermentation to produce succinic acid.

* The acidity due to this substance is stated to be immediately neutralised by the alkalinity of the water or alternatively by natural phosphates present.

BLEACHING

The bleaching of flour appears to be necessary in order to produce the whitest possible flour, for which there is a considerable demand. Colour in a flour is not always due to the presence of minute traces of offal; in some wheats the whole endosperm is coloured more or less yellowish. On keeping, this colour tends to vanish, i.e. the flour whitens, a process referred to as natural bleaching or "ageing."

Bleaching is carried out in order to accomplish in a few moments what normally takes perhaps two months. Many objections to bleaching have been put forward from time to time. Some of these are based merely on prejudice, whilst others have some real practical basis. In connection with the former, many people object to having chemicals put into their food. Did they but realise that flour itself is merely a mixture of chemicals and that all chemicals are not dangerous poisonous substances, then the objection would disappear. Indeed, to-day it has largely disappeared, except in the minds of a few, and bleaching with *selected* bodies is employed on an extensive scale.

Another criticism often levelled at bleaching is that it enables a low-grade flour to masquerade as a patent flour. In this statement there is some truth, but the lowness of the grade enters into the matter. A very low grade, containing branny particles, does not yield to ordinary bleaching treatment, since bran can only be bleached successfully with sulphur dioxide, which, for other reasons, cannot be used in the treatment of flour. There is no doubt, however, that the patent grade can be "lengthened" somewhat or alternatively a flour of 60 per cent extraction may be given the colour of a flour of 50 per cent extraction. By bleaching alone, of course, it is only the colour of higher quality flours that can be imitated; the baking qualities remain the same, unless improvers are employed as well. Originally, bleaching and improving were carried out independently. Of recent years bodies may be employed which accomplish both ends, e.g. chlorine.

The substances which are employed commonly for the bleaching of flour are as follows:

(1) nitrogen peroxide, (NO_2), bleaching only.
(2) chlorine, claimed to effect improvement as well as bleaching.
(3) nitrosyl chloride, (NOCl), used in conjunction with chlorine.
(4) nitrogen trichloride, (NCl_3), used largely diluted with air.
(5) benzoyl peroxide, $(C_6H_5CO)_2O_2$, a solid agent.

These will be dealt with briefly in turn :

Nitrogen Peroxide, (NO_2). For modes of production, see Part I, page 46. The quantity of nitrogen peroxide required to bleach, is exceedingly small, and it is used commercially largely diluted with air. The air containing the nitrogen peroxide is brought into contact with the flour in an agitator, in which the flour is lifted by means of wooden paddles and gradually driven forwards.

Nitrogen peroxide seems to act as a bleaching agent by reason of its oxidising qualities. This is practically true of all flour-bleaching agents. With water, the gas forms nitrous acid and active " atomic " oxygen, according to the equation :

$$2NO_2 + H_2O = \underset{\text{nitrous acid}}{2HNO_2} + O$$

The nitrous acid becomes immediately neutralised by basic substances in the flour forming the corresponding salt, a nitrite. Actually which nitrite is produced seems a matter of doubt. Ammonium nitrite ($NH_4.NO_2$) has been suggested, since nearly all the nitrite originally present in bleached flour vanishes on bread-making, and ammonium nitrite readily decomposes, yielding gaseous products :

$$NH_4NO_2 = N_2 + 2H_2O.$$

The " atomic " oxygen becomes available for oxidation and oxidises the colouring matter of the flour to a colourless compound. It has been shown by Dr. Monier Williams that the colouring matter present in flour is identical with a substance termed " carrotin," $C_{40}H_{56}$. This substance has been isolated by other investigators and shown to absorb oxygen readily on exposure to air, to produce a colourless compound. Thus, the natural bleaching of flour on storing

is due to the oxidation of the carrotin, since it has been shown that flour does not undergo a natural bleaching if stored in the absence of air or oxygen.

Much has been written about the harmful character of the residual nitrites left in the flour. It has, however, been fairly well established that these nitrites are quite harmless. The average amount of nitrite, calculated as sodium nitrite, to be found in commercially bleached flour is 6 to 8 parts per million parts of flour. Of this, the bulk vanishes on bread-making, so that in bread the quantity of nitrites to be found is of the order of 0·025 parts per million. The harmless character of this can be gauged from the fact that rainwater contains 1·75 parts and ham 12·5 parts $NaNO_2$ per million.*

Nitrites may be detected in flour by extracting with cold water, filtering and testing the filtrate with either a dilute solution of *m*–phenylene diamine hydrochloride when a pale brown coloration is produced, the intensity of which is proportional to the amount of nitrite present; or with Griess-Ilosvay's reagent with which a more or less intense pink coloration is produced, depending on the amount of nitrite present.†

Chlorine may be produced commercially as described in Part I, page 52, where its properties are also described. It is usually sold in steel cylinders, upon which the liquid chlorine, in the absence of water, has no effect. It is claimed that chlorine acts both as an improving agent and bleaching agent. While this may be very useful in certain instances, it may not always be desirable to bleach and improve to the same extent. Thus, in some mills it will be found that other improvers are employed in addition to the chlorine bleaching; again, where it is required to effect a considerable improvement, but little bleaching, a small quantity of flour, heavily treated with chlorine, is added to the main bulk of flour as improver.

The action of chlorine in bleaching and improving flour may be viewed in the light of the equation which represents the interaction of chlorine and water:

$$Cl_2 + H_2O = HClO + HCl$$

followed by

$$HClO + HCl = 2HCl + O$$

* *American Food Journal*, 1907.

† For details see Jago, *Technology of Bread-making*, 1921 Ed., p. 307.

Here, as with nitrogen peroxide bleaching, " atomic " oxygen is liberated which oxidises the colouring matter (carrotin) to a colourless compound. An alternative explanation is offered in the formation of a colourless dichloride, $C_{40}H_{56}Cl_2$, by union of the carrotin and chlorine. Possibly the bleaching occurs by a combination of these two processes. The second product of the interaction of chlorine and water is hydrochloric acid, and it is this agent which is responsible for the use of chlorine as an improver. On bleaching the acidity (really hydrogen ion concentration) increases, and we have seen that for a weak flour this is beneficial, since it tends to bring the gluten into the correct degree of dispersion for maximum elasticity.

Often the top grade of flour in a mill does not receive any chlorine bleaching, since its hydrogen ion concentration may be of the correct value. But the hydrogen ion concentration diminishes * as the grade gets lower and lower, so that the lower grades receive most chlorine. The amount of chlorine used varies from $\frac{1}{2}$ to 3 ounces per sack of flour according to the grade. Beyond a certain grade chlorine bleaching becomes useless, since the branny particles are not bleached ; in fact their appearance becomes more marked by the difference in colour. The method of administering the chlorine is substantially the same as with nitrogen peroxide, the quantity of chlorine and air used in the mixture being controlled by a pressure device.

Nitrosyl Chloride, NOCl, is sometimes used as a bleaching agent in conjunction with chlorine. Nitrosyl chloride may be obtained either by direct union of nitric oxide and chlorine in the presence of charcoal, or by passing a rapid stream of air through a mixture of nitric and hydrochloric acids :

$$3HCl + HNO_3 = NOCl + Cl_2 + 2H_2O$$

Thus, the air leaving the liquid contains chlorine and nitrosyl chloride. It is stated that nitrosyl chloride behaves as a very effective bleaching agent. It is used with chlorine in the ratio $\frac{1}{2}$ per cent NOCl, to $99\frac{1}{2}$ per cent chlorine.

Nitrogen Trichloride, NCl_3. This substance when pure and

* The hydrogen ion concentration must not be confused with the titratable acidity. The former falls, but the latter rises as the grade gets lower. See Appendix.

dry is explosive, but copiously diluted with moist air, it is employed as a bleaching agent. It was originally used in America, and is being introduced in this country. It may be produced by passing chlorine through an aqueous solution of ammonium chloride, whereby NCl_3 is produced, which is removed by passing a stream of air through the liquor:

$$6Cl_2 + 6H_2O = 6HCl + 6HClO$$
$$6HClO + 2NH_4Cl = 2NCl_3 + 2HCl + 6H_2O$$

The humidified air, containing from 0·1 to 0·4 per cent NCl_3, passes to an agitator, where it meets the flour. The amount of nitrogen trichloride actually used in the bleaching operation is from 2 to 7 grams per sack of flour. The nitrogen chloride probably reacts by a reversal of the mode of its production, i.e.

$$NCl_3 + 3H_2O = 3HClO + NH_3.$$

Then the hypochlorous acid loses its oxygen in the atomic condition, oxidising the colouring matter, and there remains HCl, part of which is neutralised by the ammonia and the remainder being free to increase the acidity of the flour.

Benzoyl Peroxide, $(C_6H_5CO)_2O_2$. This substance is a solid, prepared by the action of hydrogen peroxide (H_2O_2) on benzoly chloride ($C_6H_5CO.Cl$) in alkaline solution:

$$2C_6H_5CO.Cl + H_2O_2 = (C_6H_5.CO)_2O_2 + 2HCl.$$

(2HCl: taken up by the alkali)

The substance is a white crystalline compound, melting at 103° with slight explosion. It behaves as an oxidising agent. This substance is of recent introduction in the bleaching of flour, although its use for the bleaching of oils has been known for some time. It is used in admixture with calcium phosphate in order to diminish the liability of the peroxide to ignite. One of the proprietary brands of solid bleaching agent contains 25 per cent benzoyl peroxide and 75 per cent calcium phosphate. Benzoyl peroxide is a slow-acting bleacher, since it depends for its use on the slow release of oxygen by the action of water:

$$(C_6H_5CO)_2O_2 + H_2O = 2C_6H_5COOH + O$$

The " atomic " oxygen oxidises the colouring matter, carrotin, to a colourless compound in the usual way. The peroxide is used either by intimately mixing it in with the flour to be

bleached and storing it for a few days, or by mixing it in with the stock during the process of manufacture. The resulting benzoic acid left in the flour is present in only infinitesimal amounts and its effect is practically negligible.

It will be observed in connection with these bleaching and improving agents that as a class they are either oxidising agents or substances of an acid character. All the bleaching agents depend for their use upon their oxidising qualities, whilst the improvers are usually acidic bodies, bodies capable of producing other acids or bodies able to assist in the production of acid by the yeast during fermentation.

APPENDIX TO PART II

Note on Polarisation of Light. Light may be considered as a series of vibrations in the ether. The ether is the name given to the medium which is *supposed* to fill all space.

According to one of the theories of light, a ray of light may be regarded as a certain wave motion in the ether, somewhat similar to the wave motion set up in a cord fixed at one end (Fig. 52). If such a cord be shaken violently, a series of waves passes along

FIG. 52

it. Considering any one point on the cord, it will be seen that it vibrates in the direction of the plane of shaking. The disturbance in the ether set up by a light ray is really rather more complicated, and, instead of consisting merely of a series of vibrations in one direction only (as with the cord), consists of a series of vibrations in all directions in a plane at right angles to the path of the ray.

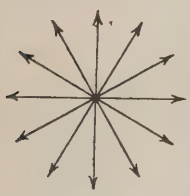


FIG. 53

If the disturbance of the ether particles could be made apparent, a view of an oncoming light ray would appear as in Fig. 53. When a crystal of Iceland spar, cut in a particular manner, is interposed in the path of a ray of light, it acts in the fashion of a sieve with parallel wires, in that it allows light consisting of vibrations in one particular direction to pass through. Thus, the light after passing through the crystal consists of a series of vibrations in one direction only. This is termed *plane polarised light*, and the direction of vibration of the particles the *plane of polarisation*. The naked eye can detect no difference between plane polarised light and ordinary light. If the polarised light be viewed through a second crystal of Iceland spar cut and placed in identical manner to the first, no change in the character of the field of view may be observed. If, on the other hand, the second crystal be rotated on its axis in a plane

at right angles to the light beam until it has been turned through an angle of 90°, then no light will pass this combination.

Referring to Fig. 54, *a* represents the vibrations of ordinary light, *b* those of light polarised in a vertical plane which may be

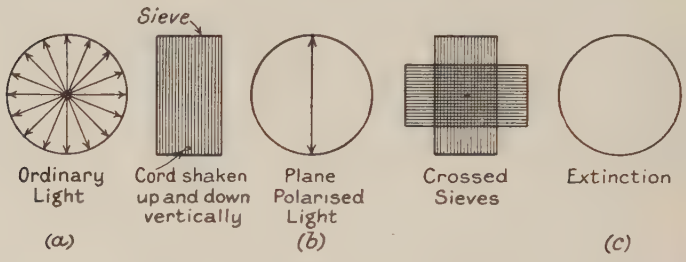


FIG. 54

compared to a point on a cord shaken up and down in a vertical plane between the parallel wires of a sieve ; *c* is the position of extinction, which may perhaps be best understood by the analogy of the crossed sieves placed at right angles to one another. It is obvious that a cord shaken up and down vertically in such an arrangement of wires will receive no wave motion and any one point on it will be at rest. This corresponds to the position of the two crystals of Iceland spar, when one is rotated so that it occupies a position with its axis at right angles to the other.

Two crystals of Iceland spar, such as have been indicated,

FIG. 55—DIAGRAMMATIC VIEW OF POLARIMETER PARTS

P Polarising crystal. *V* Rotating scale.
A Analysing crystal. *T* Telescope.

together with suitable lenses as eyepieces, form the essential parts of a "polarimeter," an instrument employed for the observation and measurement of the optical activity of such bodies as the sugars.

A substance is said to be optically active if it will rotate the plane of polarisation of the light. For observation, the substance is placed in a tube of definite length between the two crystals. The position of extinction having previously been recorded on a rotating scale without any substance in the instrument, the angle through which the second crystal must be rotated in order to give extinction again, is observed when the substance is introduced. This angle is a measure of the optical activity of the substance. The rotation may be either in a clockwise or anti-clockwise direction. A substance behaving in the former way is said to be " dextro-rotatory," and the latter " lævo-rotatory."

For further details on polarimetry the student should consult any standard work on Physics or Physical Chemistry.

Note on Hydrogen-ion Concentration. Some substances, when dissolved in water, form solutions which will allow a current of electricity to pass through them, whilst others form solutions which do not conduct electricity. The former substances are termed " electrolytes " and the latter " non-electrolytes."

In order to account for this difference in behaviour, Faraday supposed that the electrolyte exists in the solution as charged particles termed " ions," and that it is these ions which carry the electric current. In a non-electrolyte these ions are not present and no current can be passed.

Take for simple example a solution of common salt in water. A molecule of salt, NaCl, is a neutral particle, but in the presence of water splits into a positively charged sodium ion and a negatively charged chlorine ion :

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

These ions have no independent existence and cannot be isolated as such from a solution. A substance which forms ions in this way is said to be ionised in the solution, the extent to which this ionisation occurs depending on the nature of the substance.

If an electric current be passed through a salt solution, the positive Na ions move towards the negative pole. Likewise the chlorine ion moves towards the positive pole. When it reaches this its charge becomes neutralised by the charge on the pole and the chlorine appears as ordinary gaseous chlorine.

Pure water is practically non-conducting and is only feebly ionised, thus :

$$H_2O \rightleftharpoons \underset{\text{hydrogen ion}}{H^+} + \underset{\text{hydroxyl ion}}{OH^-}$$

i.e. the bulk of the water particles are present as unionised water molecules and a few are split into hydrogen ions and hydroxyl ions. Actually, the number of hydrogen ions present in a litre of pure water is $\frac{1}{10000000}$.* The number of hydroxyl ions must necessarily be the same.

All acids, which are hydrogen salts, ionise in aqueous solution to a greater or lesser extent. The extent to which they ionise has been found to be a measure of their strength or intensity of acidity or chemical reactivity as acids, e.g. a solution of hydrochloric acid containing $\frac{1}{10}$ of a gram-equivalent,† 3·65 gm. HCl, per litre is found to be over 80 per cent ionised, i.e. about 20 per cent of the hydrochloric acid is present as HCl molecules and the remainder as H ions and chlorine ions. Now $\frac{1}{10}$ of an equivalent of HCl contains $\frac{1}{10}$ or ·1 gm. of hydrogen, so that over 80 per cent of this hydrogen, viz. $\frac{80}{100} \times \cdot 1 = \cdot 08$ gm. hydrogen, is present as hydrogen ions. Thus the hydrogen ion concentration of a solution of hydrochloric acid containing $\frac{1}{10}$ of a gram-equivalent of HCl per litre is about ·08 gm. hydrogen ions per litre (actually ·084).

Acetic acid, on the other hand, is a far weaker acid than hydrochloric acid. Its chemical reactivity as an acid or acid intensity is less. A solution containing $\frac{1}{10}$ gram-equivalent of acetic acid (6 gm.) per litre is ionised only to a feeble extent, viz. 1·36 per cent.

$$CH_3{\cdot}COOH \rightleftharpoons \underset{\text{acetyl ion}}{CH_3COO^-} + H^+$$

i.e. 1·36 per cent of the replaceable hydrogen of acetic acid is present as ions and the remainder in the un-ionised condition. Thus the hydrogen ion concentration of a solution of acetic acid containing $\frac{1}{10}$ gm. equivalent of acetic acid per litre is $\frac{1{\cdot}36}{100} \times \cdot 1 =$ ·00136 gm. H ions per litre. These two quantities of acid, each

* Alternatively one hydrogen ion is present in 10,000,000 litres of water.

† Gram-equivalent = quantity in grams equivalent to or containing 1 gm. of replaceable hydrogen.

separately contains the same total quantity of replaceable hydrogen, would require the same amount of alkali to neutralise them, viz. $\frac{1}{10}$ of a gm. equivalent. But although their titratable acidity is the same, the intensity of acid is different. The hydrochloric acid is far more reactive as an acid than the acetic acid. This is attributed to the greater number of hydrogen ions in the hydrochloric acid. The hydrogen ions may be regarded as immediately available for chemical reaction, whereas the hydrogen combined in the molecule is not so readily available ; HCl has 80 per cent of its hydrogen immediately available for chemical reactions, whilst acetic acid only has 1·36 per cent of its hydrogen available ; hence the difference in acidic intensity in the two acids.

A neutral solution has a hydrogen ion concentration of 10^{-7} gm.* per litre (e.g. water), whilst if this value is increased by the addition of an acid, then the value rises as in the case of the HCl given above, to $10^{-1\cdot08}$ gm. per litre. If alkali be added to water whereby the (OH) ions increase and the H ions decrease, the value of the hydrogen ion concentration falls below 10^{-7}, e.g. 10^{-9}.

A scale has been arrived at on which hydrogen concentrations are measured, termed the p_H scale. On this scale the hydrogen ion concentration is represented as a number expressing the power of 10, when the hydrogen ions per litre are expressed in that manner. The negative sign is omitted, e.g. a hydrogen ion concentration of

$\frac{1}{10}$ gm. per litre = ·1 gm. litre = 10^{-1} represents $p_H = 1$

$\frac{1}{100}$ " " " = ·01 " " = 10^{-2} " $p_H = 2$

$\frac{1}{10000000}$ " " " = ·0000001 " " = 10^{-7} " $p_H = 7$

$\frac{1}{1000000000}$ " " " = ·000000001 " " = 10^{-9} " $p_H = 9$

Thus the more acid a liquid may be the lower its p_H value : neutrality ; $p_H = 7$; strongly alkaline $p_H = 9$; and strongly acid $p_H = 2$.

The normal p_H value of bread is of the order of 6·00, i.e. slightly acid.

According to Jessen-Hansen † the following table shows the value of the p_H and also the titratable acidity of flour and bran.

* $10^{-7} = \frac{1}{10000000}$.

† *Comptes Rendus des Travaux du Laboratoire de Carlsberg*, 1911, 10, 170.

It will be noted that the titratable acidity rises as the grade gets lower, but that the hydrogen ion concentration falls, i.e. the value of the p_H rises since it is a reciprocal :

	Flour 0 — 3% extraction	Flour 36 — 75% extraction	Brans
I. C.c. of soln. of NaOH [containing 8 gm. litre] required to neutralise 50 c.c. of extract, using phenol-phthalein as indicator	·55	·78	3·50
II. p_H	6·06	6·14	6·55

EXAMINATION PAPER OF THE CITY AND GUILDS OF LONDON INSTITUTE TECHNOLOGICAL EXAMINATIONS

Flour Milling, Final Course, 2nd year.

1929.

1. Write a short essay on starch, showing its occurrence in nature, its uses, and the way in which sugar can be obtained from it.

2. What is a protein ? State the simple chemical tests by which you would recognise a substance as a protein.

3. Distinguish between diastaste, pepsin and zymase. In what way does the behaviour of enzymes resemble catalysis ?

4. Describe the behaviour of yeast in an ordinary dough.

5. How are micro-organisms isolated and recognised ?

6. What is meant by sterilisation and how is it usually effected ?

MISCELLANEOUS QUESTIONS.

1. What is meant by the term " Strength " in relation to wheat and flour ? Write an account of the various factors which affect the " strength " of wheat and flour.

2. Write short descriptive notes of the following : (*a*) Colloidal state, (*b*) " Inversion " of Cane Sugar, (*c*) Enzymes, (*d*) Alcoholic Fermentation.

3. Explain briefly what part proteins play in the human diet. Describe how you would set about the determination of the percentage of protein in a foodstuff like flour or bread.

4. Write a short essay on the "Bleaching of Flour," embodying the need for bleaching, the methods employed, the changes occurring on bleaching, and the methods of detecting bleached flour.

5. Explain the fundamental differences between organic and inorganic compounds. Classify the chemical constituents of the wheat grain into these two classes and indicate how you would determine experimentally the percentage of either one class.

6. How would you demonstrate the presence in wheat of (*a*) a sugar, (*b*) starch, (*c*) nitrogenous compounds? Write a brief summary of the physical and chemical properties of starch.

7. In what form is moisture in the wheat grain? Indicate the precautions which must be taken in order to get concordant results for the moisture determination, and explain the necessity for some universal standard method for this determination.

8. What are the characteristic features shown by organic compounds as compared with inorganic or mineral compounds? Explain how one of these features is employed to determine the mineral matter in a sample of wheat or flour.

9. What common *classes* of organic compounds are you acquainted with? Give the characteristic feature of each class, also examples of each, indicating which of the classes is to be found in the Wheat grain.

10. Write a short account of the methods employed for the bleaching of flour. Indicate (*a*) the various substances used, (*b*) how they may be obtained, (*c*) the supposed mechanism of the bleaching, (*d*) how the bleaching may be detected.

11. What is meant by the term "strength" in connection with wheat and flour? Indicate the various factors which affect strength and mention methods which have been put forward to measure it.

12. What do you understand by the term "Humidity of the Atmosphere"? How may it be measured, and indicate how variation in humidity affects milling and the percentage of moisture in flour.

13. Write shortly on the following: Enzymes, Alcoholic Fermentation, Invert Sugar, Moisture of Constitution, Self-raising Flour.

14. Give a full account of the properties of starch, and mention how you would isolate a sample of any one starch and identify it.

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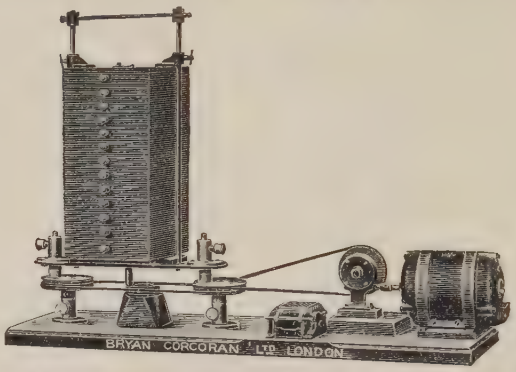

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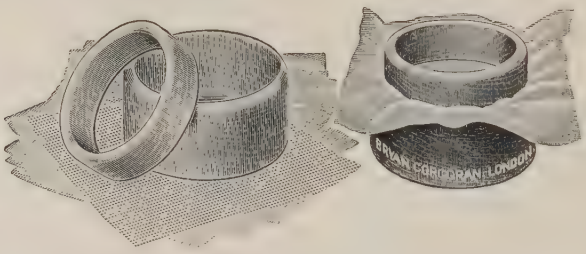

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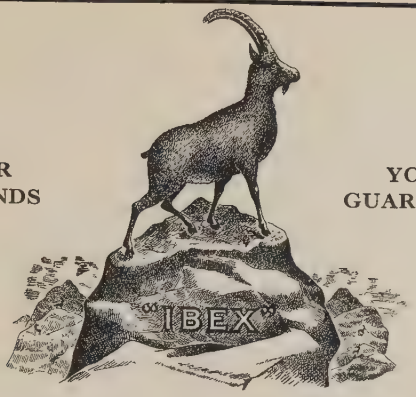

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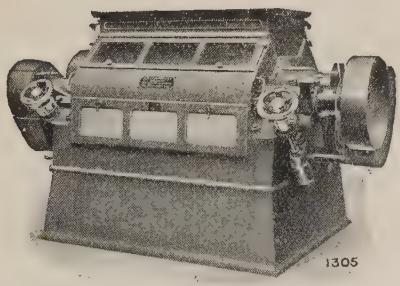

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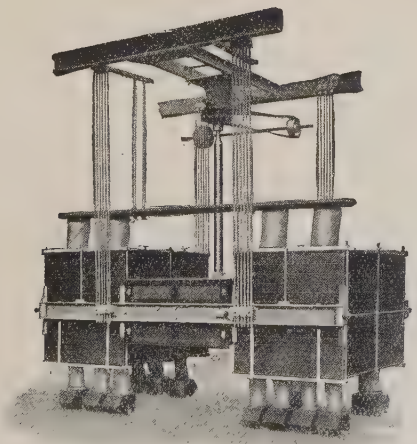

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